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NEW EVIDENCE ON THE ORIGIN OF THE CHIATURA MANGANESE DEPOSIT

G. S. DZOTSENIDZE

The Chiatura manganese deposit is widely known as a typically sedimentary deposit with large reserves of high quality ores, concentrated within a limited area.

The ores belong mainly to the three following types: *1)* primary oxides, *2)* carbonates, *3)* oxidized ores. Carbonate ores are reported from the central part of the deposit, whereas primary oxides occur in its peripheral parts.

Host rocks of the deposit are represented by opokas and spongiolites. The thick beds of bentonitic clays and clinoptilolite, revealed in the Upper Oligocene cover of the ores by the recentmost lithologic studies, suggest some volcanic ash supply to the Upper Oligocene sedimentation basin [MACHABELI *et al.*]. Quantity and grain-size of the terrigenous detritus, composing the Oligocene arcosic sandstones, increases eastward. In the eastern margin of the deposit a thick sequence of the Lower Oligocene clays and sandstones contains only few thin ore-bearing beds, but is increasingly enriched in ore-bodies towards the west and gradually displaced by the latter, so that in the western periphery of the deposit the Upper Cretaceous limestones are directly overlain by primary oxide ores, containing but an insignificant admixture of terrigenous material.

A. G. BETEKHTIN who was first to study the Chiatura deposit in detail, suggested that manganese, as well as arcosic detritus, was derived from the Paleozoic granitoids, presently exposed in vicinity of the deposit. But A. G. BETEKHTIN disregarded that manganese content of these granites is below clark (0,04%). Besides, his concept failed to explain a rapid accumulation of manganese within a comparatively short period of the Lower Oligocene; whereas weathering of granites (predominantly mechanical) proceeded during a long interval of time.

In our search for manganese source of the Chiatura deposit we came to the conclusion that manganese could be supplied only by hydrothermal solutions, that were very active in the late Upper Eocene — early Oligocene, i. e. in postvolcanic stage of an intense Paleogene volcanism of the Adjaro-Thrialethian geosyncline [DZOTSENIDZE, 1965]. The assumption was based on the neighbouring position of the Chiatura deposit to the Adjaro-Thrialethian folded system. The well known theorist of climatic types of lithogenesis N. M. STRAKHOV agrees with the present author, that granites were unable to provide the quantity of manganese accumulated in the Chiatura Oligocene basin. But he considers the Middle Jurassic spilitic series, spread north of Chiatura as a possible source of manganese, referring to the fact that manganese content of the Middle Jurassic volcanics approaches clark value (0,1%) and occasionally attains 0,4—0,5% [DZOTSENIDZE, 1948]. In this connection we would like to point out that as far as no products of the Middle Jurassic volcanic series

are present in the terrigenous rocks of the Chiatura deposit, it is rather difficult to accept this series as the possible source of manganese. Certainly, this fact should not be neglected. Besides, nobody even attempts to explain how it is possible that manganese derived from magmatic rocks during long processes of weathering and deposition accumulated in few thick ore-beds instead of being evenly distribute throughout the sedimentary sequence along with other products of weathering.

In last years new data were obtained, strongly supporting volcanic-sedimentary origin of the Chiatura and adjacent deposits. Most important among these are the results of the study of the Kvirila depression deposit, located WSW of Chiatura *(Fig. 1)*.

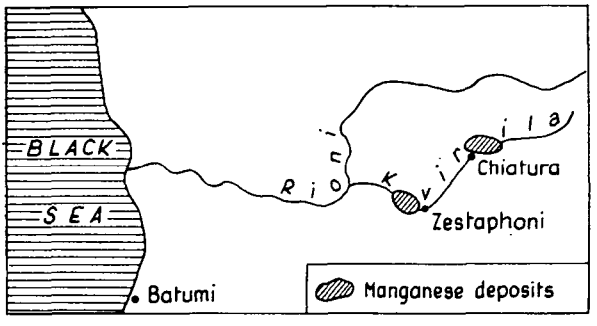

Fig. 1

Being quite similar in their general upbild, the Chiatura and Kvirila depression deposits differ by their geological setting. What are the similarities? First, either deposits occur in the Oligocene strata and are apparently closely correlative in age. Second, the section of the ore-bearing sequence in both deposits is much alike. In the Kvirila depression as in Chiatura host rocks are opokas, spongiolites, glauconitic rocks. Here, too, the ores are represented by primary oxides, carbonates and oxidized varieties. But in the Kvirila depression dominate clays of so called Maikopian type, and among them the above-named rocks form lenses of various dimensions.

The principal distinction between the Chiatura and Kvirila depression deposits is their different geological position.

The Chiatura depression is located in the elevated part of the Georgian median block, called the Dzirula mass. The latter is composed of Paleozoic granitoids, crystalline schists and quartz-porphyries. In the Lower Liassic a significant part of the mass represented dry land. From the Middle Liassic transgression of sea began and sea invaded the whole Dzirula mass. Later on, in the Middle Jurassic it became an area of the intense volcanic activity and as a result a thick spilitic series was formed [DZOTSENIDZE *et al.*, 1953]. Following uplift of the mass turned it to land, where crust of weathering developed [DZOTSENIDZE, 1963]. Invasion of the Cretaceous sea resulted in the Cretaceous sedimentary cover of the mass, represented by a horizontal sequence of limestones. A new uplift freed the Dzirula mass of sea and it remained land up to the end of the Upper Eocene. Beginning of an intense folding and uplift in the Adjaro-Thrialethian geosyncline caused migration of sea from the geosyncline towards the adjoining landmasses, including the Dzirula mass. A significant part of the latter was covered by the Oligocene sea, where the Chiatura manganese deposit was formed.

Due to the rigid substratum and horizontal Cretaceous strata the Chiatura ba-

sin of the Oligocene sea represented a depression with nearly flat bottom, favourable for deposition of the continuous layers of manganese-ores and their host rocks.

As it can be seen, the Dzirula mass experienced epeirogenetic movements. Uplift, initiated in post-Oligocene time caused an extensive erosion of the Oligocene and older rocks, including the Paleozoic basement. Erosion of Oligocene strata destroyed a significant part of the Chiatura manganese deposit.

West and East of the Dzirula mass subsidence zones occur. The Kvirila depression deposit is located within the western zone of subsidence. In difference from the Chiatura deposit, the Oligocene sediments of the latter rest upon the Upper Eocene marls. The Kvirila depression directly adjoins the northern border of the Adjaro-Thrialethian geosynclinal zone, composed mainly of the Cretaceous and Paleogene volcanic formations [DZOTSENIDZE, 1964]. Evidently, concurrently to the intense volcanism and formation of volcanic sequences in the Adjaro-Thrialethian geosyncline, marls deposited in the adjoining Kvirila basin. Pre-Oligocene folding stage that uplifted the Adjaro-Thrialethian range was reflected in the Upper Eocene sediments of the adjacent basin by formation of latitudinaly trending folds with axes parallel to the Adjaro-Thrialethian range. As a result, the Oligocene basin of the Kvirila depression was characterized by an uneven bottom with alternating synclinal troughs and anticlinal rises. In the synclines a comparatively undisturbed accumulation of manganese took place, whereas the anticlinal rises are nearly devoid of manganese layers or comprise only small ore-bodies. This accounts for highly variable thickness, rapid tapering out and nearly lenticular character of the ore-bearing horizon in the Kvirila depression. It is to be noted, that folding proceeded during the Oligocene as well and hence, the Oligocene sediments are synorogenic.

The Upper Eocene marls of the Kvirila depression contain some opal and are correctly referred to as opoka marls [A. MAKHARADZE, D. CHELIDZE]. Even single sponge spicules are present, intensely replaced by calcite. In the WSW part of the Kvirila depression the Upper Eocene marls grade laterally into sandy-argillaceous opokas, that are tuffitic in appearence because of a significant content of the fresh andesine grains.

As to the silicites represented by opokas and spongiolites, they are abundant in both the Chiatura and Kvirila depression deposits. It is very indicative that silicites are absent from the eastern part of either deposits, their thickness gradually increasing towards the West. For example, in the western margin of the Kvirila depression their thickness attains 150 m but here they grade laterally into the Upper Eocene marls. Usually spongiolites form large lenses in opokas. In both Chiatura and the Kvirila depression silicites are laterally substituted eastward by clays of so called Maikopian type, containing montmorillonite as the principal clay component.

The above data show that in certain regions silica deposition begins in the Upper Eocene and increases in the Oligocene. Thus the postvolcanic hydrothermal activity supplying silica and later on also manganese, began in the Upper Eocene and not in the Oligocene.

The single sponge spicules in the Eocene marls suggest a meagre silica supply. With increase of the silica supply an extensive accumulation of opokas begins and in some favourable areas sponges flourish and spongiolites are formed.

As it is well known, land-derived silica is appreciable in sediments, only if the latter are formed in environments of slow supply of the terrigenous detritus. Consequently, the time of the Upper-Eocene marl deposition should be most favourable for silica accumulation. But just the opposite is observed. The Upper Eocene marls

contain an insignificant amount of silica. On the contrary, accumulations of the Oligocene sandy-argillaceous sediments is accompanied by an extensive deposition of opokas, spongiolites, glauconite, montmorillonite and manganese over large areas of the basin.

This fact can be explained only by intensification of volcanic hydrothermal-activity in the late Upper Eocene and Oligocene, related to termination of the intense Eocene volcanism in the adjacent Adjaro-Thrialethian geosyncline.

Comparison of the above facts draws to the conclusion that manganese deposits of Chiatura and the Kvirila depression were formed at the bottom of the Oligocene sea, within two distinct depressions, separated by a threshold of the Cretaceous limestones. *(Fig. 2)*. Besides, the Chiatura depression was from the beginning

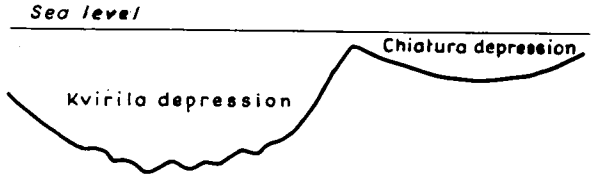

Fig. 2

situated at a higher level, as indicated by the quartzose sands and sandstones that underlay the ores. These sandstones are thickening eastward up to 25—30 m and gradually taper out towards the West. In the Kvirila depression these ore-subjacent terrigenous strata are completely absent. The Kvirila depression was gradually subsiding: this processus persisted also in the Quaternary, as it is evidenced by a thick (20 m) alluvium and puissant terraces, elevated at 80—100 m above the valley-level. In distinction from the Kvirila depression, the Chiatura depression was affected by small-scale eustatic movements, but in the Lower Oligocene, here too, subsidence prevailed, that was changed later by an intense uplift. This accounts for the fact, that the Chiatura plateau is situated presently at 500 m above the Kvirila depression *(Fig. 3)*.

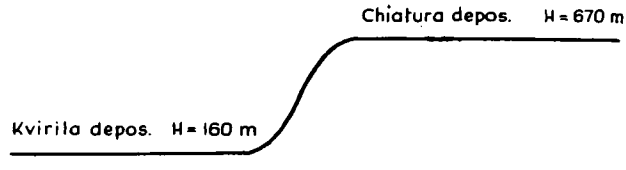

Fig. 3

An analogy with the Red Sea depressions is apparent, where hot brines deposit Cu, Zn, Pb sulfides, irone oxides, manganese, montmorillonite [DEGENS, E. and D. ROSS, 1969].

In the Red Sea depressions hydrothermal solutions rise from the depth and as we suggested [DZOTSENIDZE, 1972], they are of volcanic origin. The fact that bottom hydrothermal of the depression Atlantis-II are manifested locally and do not result from the deep migration of sea-water from the Gulf of Aden is confirmed by the new studies of the water and temperature regime in this depression [ROSS, 1972].

Presence of the silica sponges indicates that no brines existed in the depressions of the Oligocene sea. But the same fact suggests that water in these depressions was warmer than elsewhere in the Oligocene sea, as far as no sponges are found beyond their limits.

Let us consider the last and most important question of the genesis of the Oligocene manganese deposits of Georgia. What is the explanation for a strong manganese enrichment of the hydrotherms emitted at the bottom of the above depressions? Geosynclinal volcanism was active during the Jurassic and Cretaceous, but no manganese deposits are related to their postvolcanic activity.

Our approach to the problem is based on the widely known concept by V. M. GOLDSCHMIDT [1938] that many trace elements present in magma do not form their own minerals but are trapped in the crystalline lattice of the rock-forming minerals. The latter can accept in their lattice only trace elements with ionic radii compatible to those of the principal elements of the mineral.

This approach allowed the author to explain a nearly exclusive connection of the Georgian barite deposits with the Middle Jurassic volcanic series [DZOTSENIDZE, 1948, 1965]. As it is known, barium and potassium have closely compatible ionic radii and barium is isomorphous in the lattice of potassium feldspars. But as far as the Middle Jurassic volcanic rocks are nearly devoid of potassium feldspar, barium present in the melt was unable to enter rockforming minerals during crystallization, was removed by postvolcanic solutions and later formed numerous hydrothermal veins, that are widespread in the Middle Jurassic volcanic series of Transcaucasia [DZOTSENIDZE, 1945, 1948, 1960].

From the above considerations follows that manganese enrichment of the Oligocene hydrothermal solutions can be explained by the character of the Paleogene volcanic activity of the Adjaro-Thrialethian geosynclinal zone and by manganese behaviour in the magmatic melt.

The Paleogene effusive rocks of the Adjaro-Thrialethian range are represented mainly by augite porphyrites [DZOTSENIDZE, 1948], where manganese is present predominantly in the augite. The manganese content of these rocks approaches the clark value (0,1—0,15% MnO). But in the northern border of the geosyncline that is directly to the Kvirila depression and Dzirula mass, the Middle and Upper Eocene series attaining 1500—2000 m in thickness consists of potassic basalts, trachytes, trachyandesites, trachytic rocks being dominant and forming 2/3 of the whole sequence [DZOTSENIDZE, 1948, 1966; LORDKIPANIDZE, NADAREISHVILI, 1964]. Trachytes contain but minor augite and, as a result, their manganese content is 0,03—0,06%, that corresponds 1/2—1/3 part of manganese, present in the parental magmatic melt (0,1—0,15%).

Consequently, during formation of these volcanic rocks considerable amount of manganese remained in the residuum and later enriched in the postvolcanic hydrothermal solutions. It can be calculated that the quantity of manganese received by the hydrothermal solutions in this way, is to originate several deposits of Chiatura scale.

The fact, that residual manganese was removed by hydrothermal solutions is suggested by the manganese veins reported from the Middle und Upper Eocene rocks in several localities of the Adjaro-Thrialethian range.

The polarity in manganese content of effusive rocks and postvolcanic hydrothermal solutions is confirmed by some other Georgian examples: *1)* The Cretaceous dacites and albitophyres contain traces up to 0,05% of manganese. Numerous, quite intense hydrothermal manganese manifestations and deposits are related to

these rocks; *2)* the Paleocene dacites of some regions with the similarly low manganese content (up to 0,05%) also comprise manganese veins and layers; 3) a reverse example is provided by the rocks of the Middle Jurassic volcanic series. They are characterized by an elevated manganese content (from 0,12 up to 0,52%) but even minor hydrothermal manifestations of manganese are absent from the series, that is widespread over the whole Transcaucasia [DZOTSENIDZE, 1969].

We suggest that the polarity-rule of trace element contents in magmatic rocks and related hyrothermal solutions is true not solely for barium and manganese but is applicable to other trace elements. For example, BEUS [1959] demonstrated that beryllium-bearing pegmatites are related to granites characterized by a low beryllium content. The same is true for tin. Hydrothermal tin deposits appear to be connected with granites with tin content below clark.

Further investigation in this line would be of doubtless interest.

Along with manganese hydrothermal solutions supplied iron, that formed thin intercalations of iron oxides within the ore-bearing sequence, predominantly in its lower part. But the major part of iron entered glauconite, also, very abundant in the ore-bearing sequence. In certain cases glauconite forms up to 50% of the whole rock. A part of iron entered iron rich montmorillonite.

Thus, the Chiatura and Kvirila depression manganese deposits are sedimentary by origin, but their manganese and silica was supplied to the sedimentation basin by hydrothermal solutions and deposited according to the laws of chemogenous sedimentation. Consequently, the deposits should be considered as hydrothermal-sedimentary (volcanic-sedimentary) as far as principal ore-forming component is not land-derived, but is supplied by volcanic hydrothermal solutions.

It is to be pointed out that numerous examples of present-day manganese accumulation related to volcanic activities are known. Several of these examples have been described by the present author [DZOTSENIDZE, 1969].

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GEOCHEMICAL STUDY OF CLIFTON SPRING WATER, KARACHI, PAKISTAN

K. A. MALLICK, M. A. HASHMI, and I. A. KHAN

ABSTRACT

The study of Clifton spring water of Karachi county situated near the beach shows no appreciable effect of sea water in its taste and chemical composition.

Possible source for the water of spring and the constituents estimated from the spring water have been discussed. The realtive enrichment and depletion of the constituents estimated with regard to Monghopir warm spring found at a distance of about ten miles from Clifton have also been explained.

INTRODUCTION

Informations regarding the thermal and ordinary temperature springs of the Indo-Pakistan sub-continents are found in many of the records of Geological Survey of Pakistan and India. MACPHERSON [1854] and SCHLAGINTWEIT [1864] are considered pioniers in describing the springs of the sub-continent. OLDHAM [1882] published a catalogue of the hot springs known at that time. In 1950 GHOSH read his presidential address on the thermal springs of India and Pakistan in the Indian Sciences Conference. The officers of the Geological Survey of Pakistan have added useful informations on the occurrence of springs in various parts of Pakistan.

The reports of the above mentioned workers do not provide informations regarding the origin, discharge, temperature record, chemical composition, radiometric studies and therapeutic value of the springs.

The present paper is an effort to describe the physical and chemical properties of the potable water of the spring of Clifton, which is a well known beach site of Karachi Coast. Effort has also been made to discuss the origin of the water and to compare it with the warm spring water of Monghopir, situated at a distance of about ten miles south-east from Clifton spring.

The geochemical behaviour of the elements, estimated from the water of the spring has also been discussed. A comparative account of the compositional relationship between the waters of Clifton spring and that of the Monghopir spring has been given to illustrate the possible origin and compositions of Clifton spring water.

GENERAL GEOLOGY

The Clifton spring is situated at a distance of about 12 miles south west of the Karachi University Campus and is easily accessible by metalled road. The spring is about three furlongs from the beach of Clifton. The water of the spring is potable and oozes at the contact of Pliocene Shale and Sandstone. Local inhabitants use the water for drinking purpose.

The discharge of the water is slow but regular and it is not affected very much during the change of seasons. It does not show appreciable change in discharge of water even when there is no rain for a couple of years.

The rocks exposed in this area are Pliocene Shale and Sandstone. Conglomerate is also present above the sandstone, but it is said to be unconformable with the sandstone and hence younger in age *(Fig. 1)*. The dips of the beds range between 3 to 5° towards the sea.

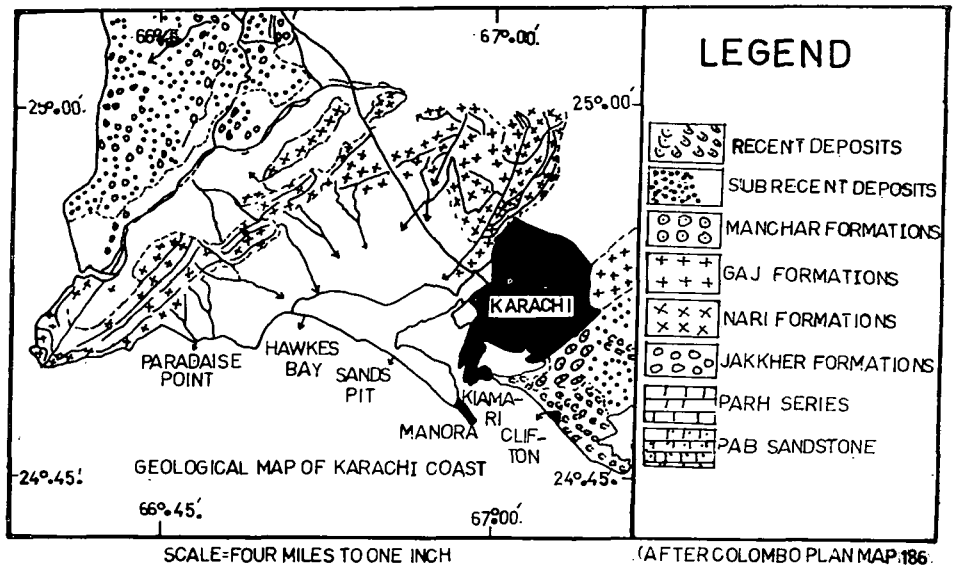

Fig. 1

The shale is light and dark grey in colour in the spring area but in other localities yellow, brown, reddish brown and yellow colour of the shale can also be seen. The thickness of the shale increases as it approaches the sea from the land. It is soft and massive in structure.

The grey sandstone is coarse to medium grained and loose in texture due to the presence of argillaceous cement. The grains are sub-rounded to rounded. The thickness of the sandstone varies from place to place but in the area under study it is 45 feet thick.

The pebbles of the overlying conglomerate is heterogenous in composition. The pebbles are mainly soft sandstone, arenaceous and argillaceous limestone similar in composition to the limestones of Oligocene and Miocene ages. Pebbles of limestone containing foraminifera are also found. The size of the pebbles is variable and ranges up to 9 inches in diameter. The pebbles are mostly angular to sub-angular.

PHYSICAL PROPERTIES

The Clifton spring is about 50 feet above sea level and the discharge of water is about 1000 gallons of water every day. The water of the spring is potable. No smell of any gas is felt in it.

The temperature, colour, turbidity, specific gravity, viscosity, refractive index

and electrical conductivity of the water is not affected appreciably with the change of seasons.

The physical properties like taste, specific gravity, surface tension, viscosity, refractive index and total hardness of the warm spring of Monghopir, situated at a distance of about 10 miles from the spring described in the present paper, show much similarities with each other. No similarities in the estimated values of temperature, turbidity, electrical conductivity etc for the Monghopir warm spring and Clifton spring could be found (Table 3). The colour of the two waters differs but the difference is not very great.

In the light of the result of chemical analysis data the Clifton Spring Water can be classified as chloride water, because the concentration of chloride (220 ppm) is much higher than the concentration of sulphate (104.06 ppm). The concentration of nitrate (0.369 ppm) and nitrite (0,024 ppm) is not very significant to name the spring water after these constituents. Phosphate, silica and hydrogen sulphide could not be estimated due to their very negligible concentration and were beyond the estimation range.

Among the metalloids and metallic radicals calcium (66.57 ppm) has got the highest relative concentration in the water of Clifton Spring. Potassium is the next

TABLE 1

Physical Properties of Clifton Spring Water

1. Temperature	27 °C
2. Turbidity	1.40
3. Odour	Odourless
4. Colour	Colourless
5. Taste	Pleasant
6. Specific gravity	1.0013
7. Surface tension	71.90
8. Viscosity	0.00787
9. Refractive index	1.3328
10. Electrical conductivity at 25 °C	0.00135
11. pH	7.6

TABLE 2

Chemical Properties of Clifton Spring Water

Contents	*Quantity (ppm)*
1. Salinity	34230.00
2. Chloride	220.00
3. Sulphate	104.06
4. Phospate	traces
5. Nitrate	0.369
6. Nitrite	0.024
7. Hydrogen sulphide	nil
8. Silica	traces
9. Oxygen absorbed at 27 °C	0.30
10. Total hardness	325.00
11. Permanent hardness	155.00
12. Temporary hardness	170.00
13. Iron (total)	0.08
14. Calcium	66.57
15. Magnesium	25.87
16. Potassium	34.44
17. Albuminoid ammonia	0.076
18. Free ammonia	0.028
19. Total solid (after evaporation)	687.00

TABLE 3

Similar Physical Properties of Monghopir Warm Spring and Clifton Spring

Characteristics	*Monghopir Warm Spring*	*Clifton Spring*
1. Odour	Odourless	Odourless
2. Colour	Live bond unit yellow	Colourless
3. pH	7.2	7.6
4. Specific gravity	1.0019	1.0013
5. Refractive index	1.3327	1.3328
6. Surface tension	70.95	71.90
7. Viscosity	0.00781	0.00787
8. Total hardness	371.5 ppm	325.0 ppm

TABLES 4

Relationship between Chemical Properties of Monghopir Warm Spring and Clifton Spring Waters

Characteristics	*Monghopir Warm Spring (ppm)*	*Clifton Spring (ppm)*
1. Chloride	600.000	220
2. Sulphate	336.69	104.06
3. Nitrate	0.369	0.369
4. Nitrite	0.001	0.024
5. Phosphate	nil	traces
6. Silica	traces	traces
7. Calcium	88.88	66.57
8. Magnesium	28.93	25.87
9. Potassium	14.50	34.44
10. Total iron	0.10	0.08
11. Consumed oxygen (at 27°C)	0.20	0.30
12. Free ammonia	0.004	9.028
13. Albuminoid ammonia	0.084	0.076
14. Hydrogen sulphide	nil	nil
15. pH	7.2	7.6

enriched in this water and its concentration is more than double of the Monghopir Warm Spring. There is slight difference in the concentration of magnesium in the waters of the two springs. The content of total iron is very low in the waters.

Similarly significant difference was found in the contents of chloride, sulphate, free ammonia, and evaporates of the two springs (Table 4).

Other characteristics like the concentrations of nitrate, phosphate, calcium, magnesium, total iron, consumed oxygen, hydrogen sulphide and the pH values of the two springs do not show any appreciable differences.

DISCUSSION

The recorded temperature of Clifton Spring Water is only 27 °C which is not very different from the normal surface temperature of a tropical region during summer season. Therefore, the calculation of depth of the reservoir, with the assumption that 1 °F of temperature increases at every 100 ft of depth in the subsurface of the earth can not be made. However, the estimated value of the temperature also can not be considered as the temperature of the reservoir. There are possibilities of

exothermic reactions between the water and the mineral constituents during accumulation of water in the reservoir and in the channel of the spring. Similarly the dessipation of heat from the spring water into the channel rocks due to the factors like porosity, permeability and chemical reactions between the water and the country rocks can not be considered beyond imagination.

Higher turbidity (1.40) as compared to the warm spring of Monghopir may be attributed to the argillaceous nature of the sandstone through which the Clifton spring water oozes. If it is supposed that higher turbidity is not due to argillaceous nature of the sandstone but it is related to chemical reactions in the substratum, then the taste of the spring water would have been saltish or bitter.

Relatively higher elevation of the spring site from the sea and the impervious Cap of Guj limestone and the shale over the Guj Sandstone forming the reservoir of the water do not allow the sea water to affect the taste of the spring water. Moreover, the waste of the ground water is also minimized.

Insignificant effect of seasonal changes on the discharge of Clifton spring water may be attributed to large catchment are, higher porosity but less effective porosity due to the presecne of clays in the reservoir rock, the overlying shale working as cap rock, gentle slope of the beds towards the sea and tectonically less disturbed condition of the area. The above mentioned factors do not allow the water to go waste and thus regular supply of water persists throughout the years.

The lower content of sulphate in the water of Clifton Spring (104.06 ppm) as compared to Monghopir Warm Spring (336.69 ppm) is probably due to common occurrence of gypsum in the Nari shale which decomposes after coming in contact with warm water (38 °C) of the spring. The decomposition of gypsum is expected to affects the concentration of Ca also in the spring water but the content of calcium estimated does not show any marked difference in this connection. The insignificant difference between the contents of calcium in the two spring water may be probably because of the highly sensitive nature of calcium in solution and precipitation environments.

Magnesium does not show any significant change in its mobility with respect to the differences in temperature and the magnitude of depth which causes difference in pressure through the channels of the water of the two springs.

The higher concentration of potassium in the water of Clifton Spring (34.44) as compared to Monghopir Warm Spring (14.56) requires more work to put forward any logical arguments or to explain its geochemical behaviour in the areas of the present study.

It could be postulated that though the rocks encountered in the Clifton spring area are the same as in the upper part of Monghopir Spring, but the former area is a coastal region and it has emerged from sea much after the emergence of the later region, therefore, it may be considered as one of the cause of higher concentration of potassium in the water. The Clifton area is saline and water logged and because the salts of potassium are more soluble and stable in solution form, so the solution of potassium could have been reaching the ground water and thus the concentration of potassium is higher in the water of Clifton Spring.

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THE TECTONIC REGIONING OF THE BASEMENT ROCKS OF THE EASTERN DESERT OF EGYPT

M. F. EL RAMLY and G. J. SALLOUM

ABSTRACT

The basement rocks of the Eastern Desert of Egypt represent a Proterozoic eugeosynclinal system. This system is the northern part of a vast geosynclinal belt which extends southwards into the Ethiopean plateau. It is divided into three major geosynclinal zones, namely: *a)* Wadi Allaqi-Wadi Kharit zone, with Gebel Holwa-Gebel Seiga-Gebel Nigrub, and Gebel Migif — Gebel Hafafit median masses in its southern and northern parts, respectively, *b)* Wadi El Miyah — Wadi Atalla geosynclinal zone, which includes Gebel Meatiq median mass, and *c)* Wadi Belih — Wadi Hawashiya geosynclinal zone. These zones are generally bordered by deep-seated faults, and are separated from each other by Gebel Abu Diab and Gebel El Shayeb geoanticlinal zones. The median masses are probably Archean-Lower Proterozoic, and might have existed prior to the Proterozoic eugeosynclinal system.

This tectonic regioning is based on the results of the regional geological mapping programs, field observations of the authors, the distribution and lithology of the different rock formations and their structural relations, as well as the geomorphological features of the area under consideration.

INTRODUCTION

The construction of a tectonic framework, and consequently a tectonic map for an area is an essential step in the preparation for mineral exploration programs. This is evident, since certain groups of mineral and ore deposits are formed under special tectonic conditions or within a specific structural pattern. In addition, tectonic regioning is also of scientific interest where it may help in the study of the development and evolution of the Earth's crust as a whole, or a specific structure within it.

The absence of such a tectonic regioning for the basement rocks of the Eastern Desert of Egypt was the reason behind the non-representation of its structures on the tectonic maps of Egypt presented by SIGAEV [1959], and SIGAEV and SALLOUM [1971].

The present study is a first step in the delineation of the main tectonic features of this area. Such a study, may lead in the future to the construction of a detailed tectonic map for the Eastern Desert.

The general characteristics and relationships of the basement rocks of the Eastern Desert, their geological history, the lithology of the different formations, as well as the wide distribution of magmatism and plutonism may indicate that this area belongs to a geosynclinal system. This system extends for about 800 km in Egypt, and continues southwards into the Sudan. Its width ranges from 260 km in its southern parts to about 10 km at the extreme north. This system is believed to be the northern part of an extensive geosynclinal belt which extends southwards into the Ethiopean plateau.

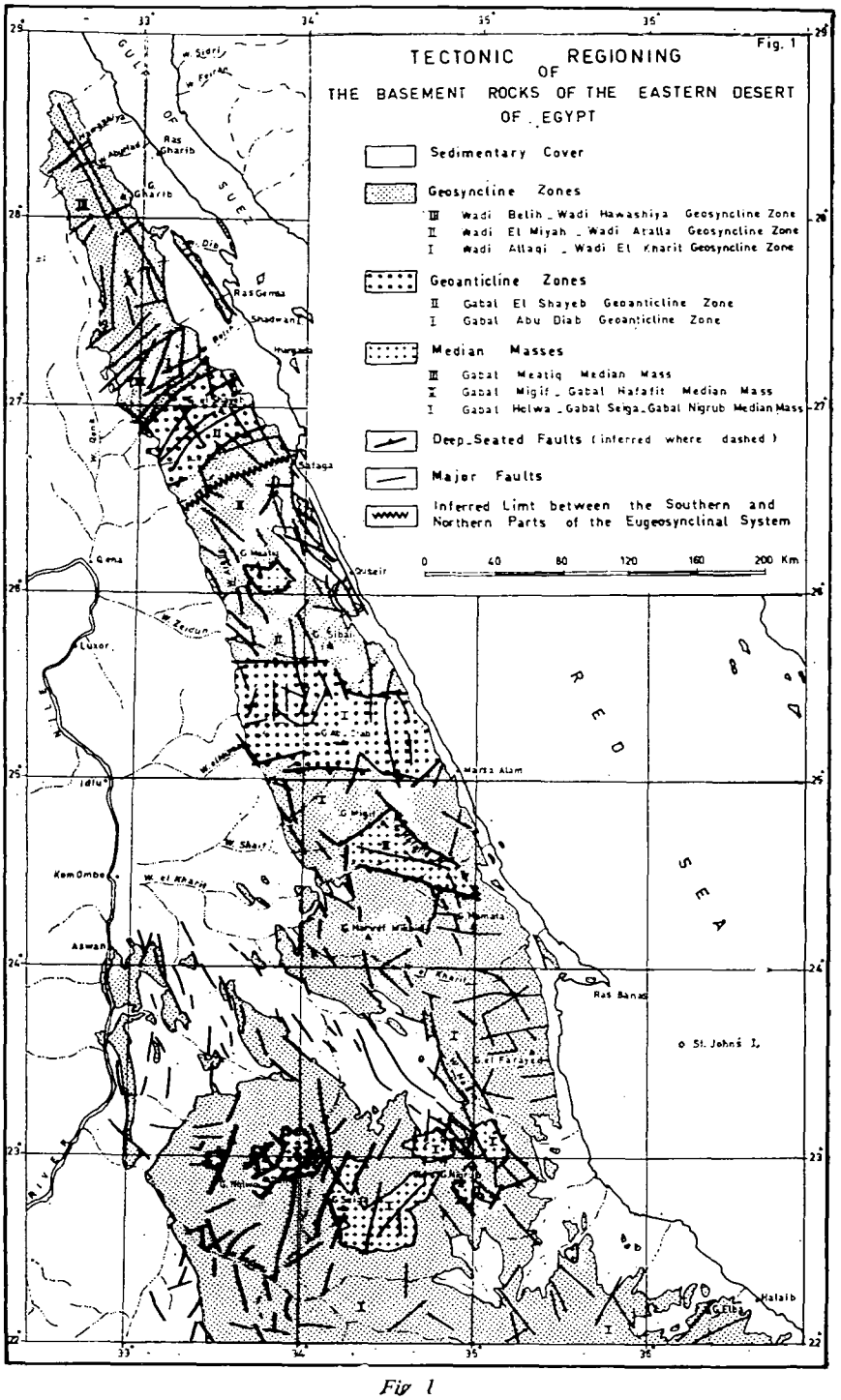
TECTONIC REGIONING OF THE BASEMENT ROCKS OF THE EASTERN DESERT OF EGYPT
Fig. 1
Sedimentary Cover
Geosyncline Zones
III Wadi Belih _ Wadi Hawashiya Geosyncline Zone
II Wadi El Miyah _ Wadi Atalla Geosyncline Zone
I Wadi Allaqi _ Wadi El Kharit Geosyncline Zone
Geoanticline Zones
II Gabal El Shayeb Geoanticline Zone
I Gabal Abu Diab Geoanticline Zone
Median Masses
III Gabal Meatiq Median Mass
II Gabal Migif _ Gabal Hafafit Median Mass
I Gabal Helwa _ Gabal Seiga _ Gabal Nigrub Median Mass
Deep-Seated Faults (inferred where dashed)
Major Faults
Inferred Limt between the Southern and Northern Parts of the Eugeosynclinal System
0 40 80 120 160 200 Km
RED SEA
Ras Gharib
Ras Gemsa
Safaga
Qusair
Luxor
Idfu
Kom Ombo
Aswan
Marsa Alam
Ras Banas
St. Johns I.
Halaib
Gebeb

Fig 1

Before going into the tectonic regioning of the basement rocks, it may be useful to give in few words, the concepts of some of the terms used here.

A geosynclinal mobile belt is one of the most important megastructures in the Earth's crust. It is characterized by maximum tectonic activity, and forms the foundation over which other structural types of the continental crust such as the platforms, epiplatforms, geoanticlinal mobile zones and others, may be superimposed. It is always limited on both sides by two old continental platforms or a continental and an oceanic platform. Its development took place during an extensive megacycle and at different ages, moreover some of its parts may pass into platformal conditions. The whole Tythean belt which is bordered by the Russian and African platforms is an example. The geosynclinal belt may include several geosynclinal systems, each of which reaches 1000—3000 km in length and 200—5000 km in width. These geosynclinal systems in their turn, include some comparatively smaller basins and uplifts, referred to as the geosynclinal and geoanticlinal zones, respectively. Primary, or orthogeosynclines were classified by STILLE [1940] into eugeosynclines and miogeosynclines. Both types differ in their evolution, history of development and intensity of magmatic activity. Generally speaking the eugeosynclines are more mobile, better developed and characterized by more intense magmatism or polymagmatism including an initial phase, mainly of basic and ultrabasic volcanism, a synorogenic phase essentially of granitoid plutons and a post-orogenic phase represented mainly by dykes.

Deep-seated faults play an important role in the development of the geosynclinal systems. They are characterized by their great depth of penetration and hence their connection with deep magmatic activities [PEYVE, 1945], their repeated rejuvenation and their surface extension for long distances. Their zones of activity usually range from 1 to 3 km across the strike but may reach up to 5 or 6 km. It is believed that the initiation and further development of any geosynclinal system is genetically connected with the presence of deep-seated faults, along which separate blocks or mozaics of the Earth's crust may move giving rise to the different structural elements of the geosyncline. Moreover, the movement of these blocks is usually governed by major regional structural trands.

THE TECTONIC REGIONING OF THE BASEMENT ROCKS OF THE EASTERN DESERT

The tectonic regioning of the basement rocks is based on the regional geological maps presented mainly by members of the staff of the Geological Survey of Egypt and partly by some other organizations ,as well as some field observations by the authors. The tectonic regioning was facilitated by the compilation of the geological map of the Eastern Desert on the scale of 1:1,000,000 carried out by EL RAMLY [1972]. Admittedly, this tectonic regioning is a generalized one. A better and more detailed picture may be constructed in the future, with the accumulation of more detailed information allowing the exact locations, sizes and degree of complication of the different structural elements involved. Boundaries between the different structural elements along the deep-seated faults are given tentatively. Their original positions are difficult to recognize because of the later intrusion and effusion of huge magmatic bodies. Also, some of them may be concealed below younger sediments. According to MOURATOV [1963], regioning of the Proterozoic geosynclines is based on their main rocks which were formed during the pre-orogenic stage of their deve-

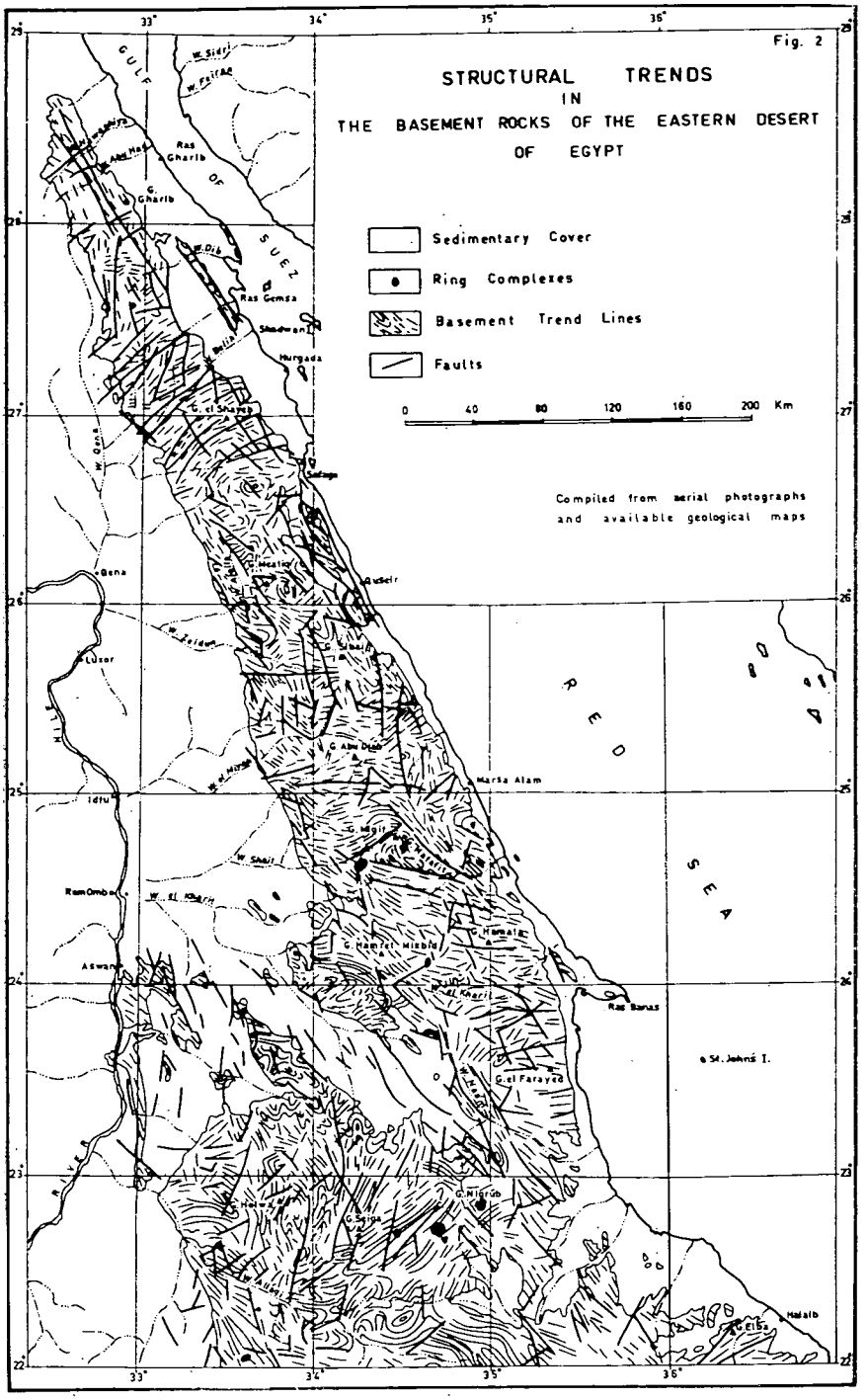
Fig. 2
STRUCTURAL TRENDS
IN
THE BASEMENT ROCKS OF THE EASTERN DESERT
OF EGYPT
Sedimentary Cover
Ring Complexes
Basement Trend Lines
Faults
0 40 80 120 160 200 Km
Compiled from aerial photographs
and available geological maps
GULF OF SUEZ
RED SEA
Ras Gharib
G. Gharib
Ras Gemsa
Hurgada
Safaga
Qena
Luxor
Idfu
Kom Ombo
Aswan
Marsa Alam
Ras Banas
St. Johns I.
G. Shayib
G. Hamrat Mizeina
G. el Farayed
G. Nigrob
G. Sarga
Halaib
33°
34°
35°
36°
22°
23°
24°
25°
26°
27°
28°
29°

Fig. 2

lopment. In the present case, the complex of rocks formed before the effusion of the Dokhan volcanics were taken as the basis for regioning. The geosynclinal system forming the basement rocks in the Eastern Desert is characterized by:

1) The high mobility of the Earth's crust.
2) The pronounced activity of magmatic intrusions and effusions or its polymagmatism.
3) The predominance of spilitic-keratophyric and prophyritic formations.
4) The original thick sedimentary sequence which at Gebel El Sibai, for example, reaches a thickness of about 7.7 km [SABET, 1961].
5) The absence of regional unconformities within this sedimentary series.

These characteristic features indicate that, this system conforms with the eugeosyncline or internal zone of the orthogeosyncline as defined by STILLE [1940].

The northern part of the eugeosyncline, north of the Latitude 26° 30′ has certain characteristics of its own. These are:

1) The predominance of granite-granodiorite plutons which form about 90% of the exposed basement rocks. These were intruded mainly in the orogenic and post-orogenic stages of the eugeosyncline.
2) In the pre-orogenic stage the magmatic activity was compartively less than that in the internal zone to the south.
3) Basic and ultrabasic intrusions are comparatively rare.

These particular characteristics made it possible to divide the eugeosyncline into two parts, a southern or internal zone and a northern or external zone *(Fig. 1)*. The border-line between these two zones is inferred, and is located just to the north of the Latitude 26° 30′.

Concerning the main structural features of the eugeosyncline as a whole, the following two main points may be noted:

1) The metasediments are generally thrown into fold mainly of the linear Alpine type.
2) Many of the wadis were eroded along fault planes, as indicated by the brecciation of the rocks forming the margins of these wadis.

Fig. 2 shows the major regional structural trends of the eugeosynclinal system of the Eastern Desert, which indicate clearly the mozaic structure of the Earth's crust within this area. These mozaics are separated from each other by deep-seated faults which may extend for considerable distances both along the strike and in depth. The exact locations of these deep-seated faults and the depth to which they penetrate are not known with certainty due to the lack of detailed structural-geophysical data, particularly aeromagnetic, over most of the area. The faults show frequent rejuvenation, in fact some of them may be in a stage of reactivation at present. Their inferred locations are shown on *Fig. 1*.

Based upon the available data, the *Proterozoic eugeosyncline*, can be divided into the following structural units from south to north *(Fig. 1)*.

1) Wadi Allaqi—Wadi Kharit geosynclinal zone which includes Gebel Holwa — Gebel Seiga — Gebel Nigrub median mass in its southern part and Gebel Migif — Gebel Hafafit median mass in its northern part.
2) Gebel Abu Diab geoanticlinal zone.

3) Wadi El Miyah — Wadi Attala geosynclinal zone, which includes Gebel Meatiq median mass.
4) Gebel El Shayeb geoanticlinal zone.
5) Wadi Belih — Wadi Hawashiya geosynclinal zone.

In naming these zones, a geosynclinal zone was named after the main wadis in the corresponding area, whereas a geoanticlinal zone was named after the highest mountain (Gebel) within the zone. Names of the median masses correspond to the main mountains within its limits.

To sum up, the eugeosynclinal system of the Eastern Desert is divided by two comparatively narrow geoanticlinal zones namely Gebel Abu Diab and Gebel El Shayeb into three major geosynclinal zones; Wadi Allaqi — Wadi Kharit, Wadi El Miyah — Wadi Atalla and Wadi Belih— Wadi Hawashiya geosynclinal zones. In addition to these two major structural elements, a third type namely the median masses is also encountered within the geosynclinal zones. These median masses are Gebel Holwa — Gebel Seiqa — Gebel Nigrub, Gebel Migif — Gebel Hafafit and Gebel Meatiq. The main tectonic features of each of these structural elements is given below.

1. Geosynclinal zones

As defined by SHATSKY [1946], geosynclinal zones are simple syncline-like forms which were subjected to a prolonged period of sinking that resulted in the accumulation of very thick bodies of sedimentary and magmatic rocks.

a) Wadi Allaqi — Wadi Kharit geosynclinal zone: This zone extends for about 330 km with a maximum width of 260 km. It represents a trough filled with a thick sedimentary sequence (now metamorphosed into the metasediments), submarine volcanics and volcanic intrusions of varying composition. The major structural trends in this geosynclinal zone are complicated. In the area around Wadi Allaqi, they predominantly follow a roughly NE—SW direction *(Fig. 2)*, whereas in the area south of the Migif — Hafafit range, they have an essentially NW—SE trend. Moreover, in the area of Gabal El Farayid and further north, they trend in an E—W direction.

b) Wadi El Miyah — Wadi Atalla geosynclinal zone: This zone is 170 km in length and its maximum width is about 100 km. The major structural trends here, follow a NNW—SSE direction.

c) Wadi Belih — Wadi Hawashiya geosynclinal zone: This zone is about 200 km in length with a maximum width of about 70 km. This width decreases down to about 10 km at its extreme northern part. The major structural trends in its northern part have an almost NNW—SSE direction, whereas in its southern part they follow a NE—SW directions.

2. Geoanticlinal Zones

Geoanticlinal zones represent the positive analogy of the geosynclinal ones [SHATSKY, 1946]. They are characterized by the relatively small thickness of their sequences and the presence of disconformities, differing in this respect from the geosynclinal zones which attain tremendous thicknesses and show no disconformities. The geoanticlinal zones are comparatively high areas which suffered from prolonged local uplifting during different geological ages and consequently they represent areas of erosion or areas of source material. They were intensively folded and the folds

were dissected by sets of major and minor faults. Their rocks are generally dynamically metamorphosed. The geoanticlinal zones are usually separated from the adjacent geosynclinal ones by deep-seated faults along which huge amounts of submarine volcanic material were effused in the initial phase, and extensive masses of granitic rocks were intruded in the final phase of development of the eugeosynclinal system of the Eastern Desert. The main geoanticlinal zones in the area are:

a) Gebel Abu Diab geoanticlinal zone: This is composed of highly deformed granitic rocks with large masses of metavolcanics and metasediments thrown into a series of complex folds and further complicated by a system of faults. The major structural trends have a sublatitudinal direction. Gebel Abu Diab geoanticlinal zone is bordered from the north and south by deep-seated faults *(Fig. 1)*.

b) Gebel El Shayeb geoanticlinal zone: This zone includes Gebel El Shayeb, the highest mountain in the Eastern Desert (2184 m). The rocks outcropping here are mainly of granitic compositon, that suffered intense deformation during the evolution of this zone. Moreover, the sedimentary and volcanic formations present, were subjected to intensive weathering. The zone is bound by deep-seated faults from the north and south. The prevailing major structural trends follow an ENE—WSW direction.

3. Median Masses

Median masses play an important role in the development of the geosynclinal belts or systems. They differ from the geosynclinal and geoanticlinal zones not only in the rock types forming them or the degree of metamorphism to which they were subjected, but also in the fact that they belong to another major and older structure, which was formed prior to the present geosynclinal system. Their general characteristics were given by ARKHANGELSKY [1939], SHATSKY [1946] and KHAIN [1964] as follows:

i) They represent remnants of old platforms of highly consolidated parts of an older folded structure.
ii) They are stable and comparatively elevated masses within a mobile geosynclinal system.
iii) Their rocks suffered intensive regional and/or depth metamorphism.
iv) The form and shape of the median masses vary from nearly rounded or angular, to almost oval or almond-shaped in outline.
v) The formations of the geosynclinal system almost encircle the median masses leaving them as islands acting as the source area for the filling of the surrounding geosynclinal troughs.
vi) Median masses are usually bordered by deep-seated faults.

In the Eastern Desert of Egypt, three major median masses are encountered *(Fig. 1)*, these are:

a) Gebel Holwa — Gebel Seiga — Gebel Nigrub.
b) Gebel Migif — Gebel Hafafit.
c) Gebel Meatiq.

The pre-existing major median masses were broken up by systems of faults into separate blocks parts of which from the outcropping median masses of the Eastern Desert. Along these faults graben-like depressions were formed, filled with later geosynclinal formations. The general characteristics of these masses may be inferred

from the best studied among them, namely Gebel Migif — Gebel Hafafit median mass. The unpublished map (scale 1:40 000) prepared by EL RAMLY shows this area to consist of a thick (4.2 km) succession of gneisses in the form of an eroded doubly plunging anticline some 55 km long and about 17 km wide. The succession of these gneisses is as follows:

Youngest

Dark green hornblende gneisses	1200 m
Grey biotite gneisses	800 m
Pinkish and grey psammitic gneisses	1000 m
Dark grey biotite-hornblende gneisses	500 m
Hornblende gneisses	400 m
Migmatitic gneisses	

Oldest

These rocks are mainly paragneisses metamorphosed after pelites, semipelites, calcareous pelites, psammites and marls. They are bordered from the north and east by a group of metasediments of a comparatively lower grade of metamorphism, including phyllites, meta-mudstones, meta-greywackes, schists and occasional conglomerates. The contacts examined, so far, between the gneisses and the surrounding meta-sediments do not reveal any obvious unconformity. Yet, there are considerable differences in lithology and degree of metamorphism that cannot be disregarded. Thus, it may be stated that the contact are of tectonic origin and follow deep-seated faults.

Gebel Meatiq median mass is mainly formed of paragneisses with some orthogneisses developed after intrusive rocks [AKAAD and SHAZLY, 1972 and SCHURMANN, 1966].

It may be generalized that the three median masses encountered in the eugeosynclinal system, were subjected to a high grade depth metamorphism and were intensively deformed. They probably belong to one and the same geological age presumably the Archean-Lower Proterozoic. They are bordered by deep-seated faults which are concealed in some places. Regional metamorphism accompanied by tectonic movements along these deep-seated faults affected the complex of formations developed later on, and gave rise to phyllites and schists which bound the median masses. Folds within the median masses are essentially domes, with few of the linear type. On the other hand, those of the eugeosynclinal system are mainly of the linear Alpine type.

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THE RELATION BETWEEN THE GEOCHEMISTRY AND DEEP-SEATED FAULTS OF ACID PLUTONITES OF EGYPT

A. A. EL SOKKARY and G. M. SALLOUM

ABSTRACT

On the basis of the present study, Egyptian granites occurring in the basement rocks are found to comprise mainly six groups, these are: Shaitian, grey, normal pink-red, strongly differentiated pink-red, anomalous pink and Aswan granites. Each of these groups has its own geochemical and structural characteristics that make it distinguishable from the others. Shaitian granites are definitely the oldest, while Aswan granites are probably the youngest.

To the first time, it is now possible to distinguish, particularly in the field, between the normal pink-red granites (pre- or syn-Hammamat) and the strongly differentiated members (post-Hammamat) previously regarded as one group of rocks. The former are found to be usually emplaced on latitudinal system of deep-seated faults (EN-WS), while the latter have generally longitudinal trends of faults (NW-SE). Chemically, these two groups of granites are related to each other by differentiation in a sense that the pre- or syn-Hammamat members represent normal granites while the post-Hammamat rocks represent their strongly fractionated members.

INTRODUCTION

The study of the geochemistry of Egyptian granites [EL SOKKARY ,1970] outcropping in the basement rocks of the eastern desert and Sinai peninsula revealed that these granites are composed of several types with distinctive chemical characters. Moreover, the so-called younger pink and red granites formerly considered as one group of rocks, were shown to comprise on chemical basis two types: a normal type beside a strongly differentiated granite type.

SCHURMANN [1966] divided the mentioned younger pink and red granites into two cycles: an older pre-Hammamat and a younger post-Hammamat cycle. Later on, EL SHAZLY, EL SOKKARY and KHALIL [1971] showed that the pink-red granites started to be developed during a later phase of sedimentation of the Hammamat group and continued after them. Thus both SCHURMANN and EL SHAZLY *et al.* agree that the pink-red granites fall into two categories: on either older or contemporaneous with Hammamat group and the other is younger than that. However, these two groups of pink-red granites could not be distinguished from each other in the field.

EL SAHZLY, EL SOKKARY and KHALIL [1972] reached to a conclusion that Wadi Shait plagioclase granite is the oldest among the earlier granites. This gives the impression that the latter granites fall into two groups: the older is the shaitian granite group, while the relatively younger are the so-called grey granites. These two types of granites were used not to be distinguished from each other and were put in one group known as grey granites [AKKAD and EL RAMLY, 1960]. However,

field relations are still wanted in order to distinguish decisively these two types of granites.

The above exposition reveals clearly that there are several types of granites that can be correlated with different stages of development of the Precambrian — Early Palaeozoic geosyncline comprising the basement rocks of Egypt. The tectonic evolution of this geosyncline was investigated recently by EL RAMLY and SALLOUM [1973]. It was thought that studying the relation between the geochemistry of acid plutonites and their geotectonic evolution might help in distinguishing clearly the different acid plutonic cycles from each other particularly in the field. This in turn will help in understanding the development of the basement rocks of Egypt in a better way.

This research possibly represents the first treatment including the relation between the geochemistry of acid plutonites and deep seated faults in the basement rocks of Sinai peninsula, eastern and south western deserts of Egypt.

TECHNIQUES

Most of the analytical data on granitic rocks are taken from EL SOKKARY [1970]. Additional data are taken from HASHAD *et al.* [1971] and unpublished work by EL SOKKARY *et al.* [1973]. Analytical data on the granite pebbles from Hammamat group and from metamorphosed geosynclinal sediments are taken from EL SHAZLY, EL EL SOKKARY and KHALIL [1971, 1972]. On the other hand, geochronological estimates are those of HASHAD *et al.* [1971] and EL RAMLY [1962].

Azimuth of deep seated faults in proximity with corresponding granitic masses are measured mainly from the geologic map of Egypt with scale 1:1000,000 recently compiled by EL RAMLY [1972].

The same map is used in measuring the total areas of basement rocks, older granites (shaitian and grey types) beside younger pink-red granites outcropping in the eastern desert only. This is done by means of a planimeter. Thus, a quantitative estimate can be obtained concering the size of all granites relative to that of basement rocks, beside a separate estimate about the sizes of the two main cycles of granites: the older and the younger granitic cycles.

PRESENTATION OF DATA

Calculations done by the planimeter revealed that the total area of outcropping basement rocks in the eastern desert is 85,600 km^2, while the respective areas of both old and younger granitoids are: 25,620 and 19,180 km^2. Thus about 29.9% of the mentioned basement rocks are represented by old granites, while 22.4% are represented by younger granites. The total area of granites represents 52,3% of the measured basement rocks. The problem of basement rocks of Egypt is therefore largely the problem of granites they contain.

Table 1 shows some important granite masses arranged in groups on geochemical-structural basis. For the individual masses, The table gives the azimuth of nearby deep seated faults, some pertinent trace elements data beside some available geochronological data. The same table includes, for comparative purposes, the analytical data on the pink granite pebbles from Hammamat conglomerates beside those data on the granite pebbles from the geosynclinal sediments. Among major and

trace elements data, EL SOKKARY [1970] showed that Ba, Sr and Rb (particularly Sr) are the most sensitive elements responding for changes in the physicochemical enviroments of granites.

Fig. 1 is a map showing the various granite masses occurring in the basement rocks of Egypt as related to corresponding deep seated faults, besides it outlines the

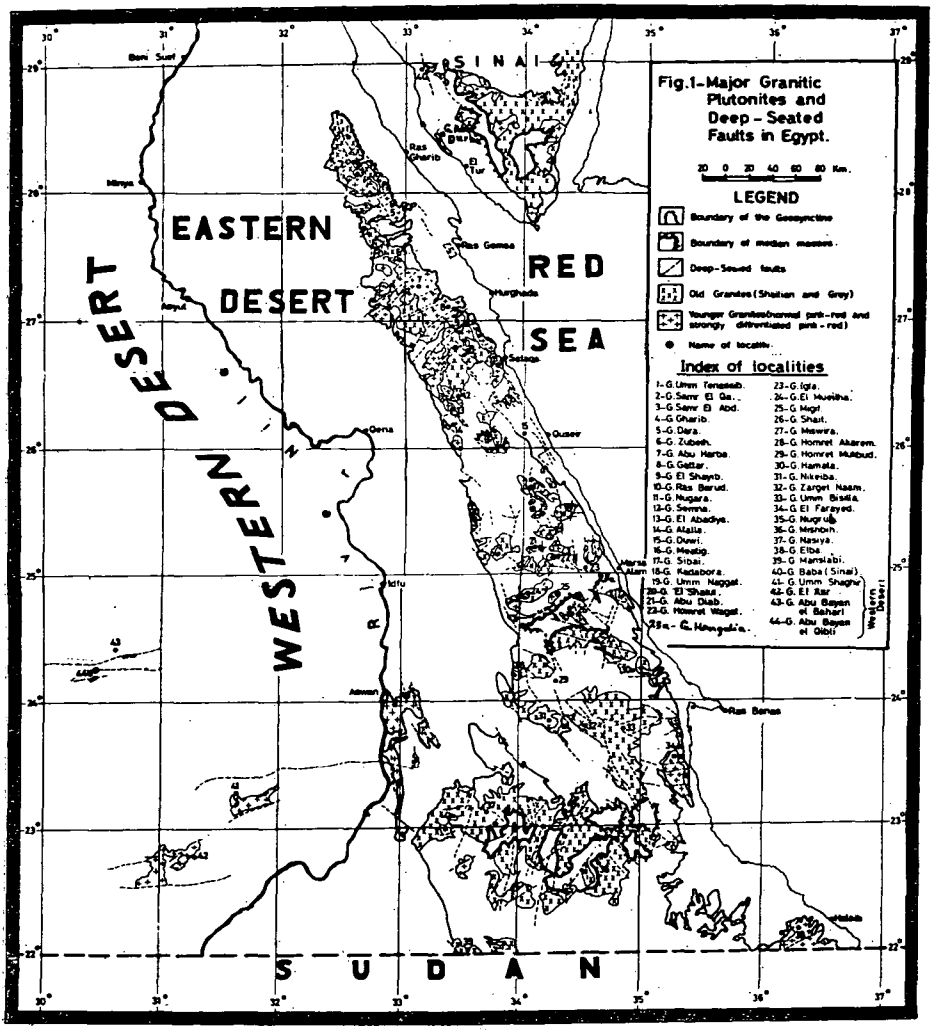

Fig. 1

terrains of median masses with which are associated the oldest granites (Shaitian) [1]. *Fig. 2* is a diagrammatic representation between the azimuth of deep seated faults of acid plutonites and their geochemistry as represented by the Sr content in ppm.

(1) It is to be noted that minor granite masses de not appear on the map.

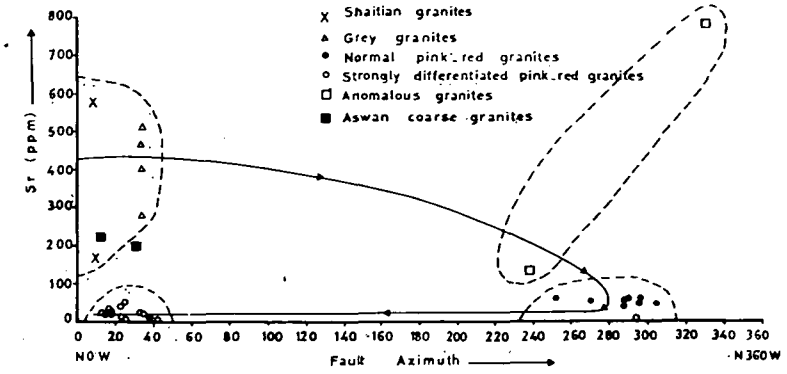

Fig.2. Relation between the azimuth of deep seated faults and Sr content (ppm) of some acid plutonites in Egypt.

TABLE 1

The azimuth of faults, trace elements data and age of some important granite masses grouped on geochemical-structural basis

Granite Type	*Locality*	*Fault Azimuth*		*Trace Elements* ppm			*Age* (m. y.)
		Measured	Converted	Ba	Sr	Rb	
Shaitian (Related to Median Masses)	G.* Shait	N8W	N8W	440	158	20	865
	W.** Baba, Sinai	N8W	N8W	635	578	76	
	Qift—Quseir (pebble)			263	216	21	
	Qift—Quseir (pebble)			1125	444	24	
Grey (Related to Geosynclinal Structure)	El Sibai Area	N33W	N33W	660	268	45	
	El Sibai Area	N33W	N33W	410	462	52	
	El Sibai Area	N33W	N33W	620	510	26	
	El Sibai Area	N33W	N33W	400	396	24	
Normal Pink—Red Pre- or Syn-Hammamat (Latitudinal)	G. Kadabora	EON	N270W	634	48	112	
		E18N	N288W	635	48	112	
	G. Elba	E26N	N296W	700	40	100	
	G. Igla	E18S	N252W	900	56	6	621
	G. Hangalia	E34N	N304W	485	44	130	
	G. Atalla	N38W	N38W	795	14	231	
	G. Abu Diab	E18N	N288W	N.D.	***35	164	533
					N. D.	26	220
	G. Siwiqat El Arsha	E20N	N290W	N. D.	51	130	515
		E35N	N305W				
		E25N	N295W				
		E34N	N304W				
	W. Kalawi (pebble)			373	58	172	
	W. Kalawi (pebble)			557	35	72	

* G. = Gebel, an Arabic Word for a mountain.
*** W. = Wadi, an Arabic Word for a valley.
*** N. D. = Not Determined.

TABLE I

Continued

Granite Type	*Locality*	*Fault Azimuth*		*Trace Elements* ppm			*Age* (m. y.)
		Measur-ed	Convert-ed	Ba	Sr	Rb	
Strongly Differentiated Pink—Red Post—Hammamat (Longitudinal)	G. El Sibai	N22W	N22W	80	13	136	
		N22W	N22W	175	36	124	
	Um Negat	N23W	N23W	49	5	228	
		N22W	N22W	62	15	226	
	G. El Muelha	N17W	N17W	57	17	154	
	G. Gattar	E24N	N294W	132	6	164	
	W. Um Dubr	N17W	N17W	N. D.	20	662	
	G. Abu Tyour	N24W	N24W	N. D.	48	90	488
	G. Homret Wagat	N14W	N14W	N.D.	7	100	
		N43W	N43W	N.D.	6	103	
	G. Homret Akarem	N17W	N17W	N.D.	20	662	
	G. El Atawi	N16W	N16W	N.D.	21	161	
		N14W	N14W				
		N35W	N35W				
		N33W	N33W				
Anomalous Pink	G. Abu Durba, Sinai	N29E	N331W	1445	776	52	
	G. Zarget El—Naam	E32S	N238W	565	125	112	
Aswan (Youngest)	Aswan Coarse	N10W	N10W	1075	223	96	470,
	Aswan Coarse	N30W	N30W	*1625*	*195*	92	*(950)*
		N27W	N26W				
		N20E	N340W				

DISCUSSION

Table 1 includes six principal granitic groups found in the basement rocks of Egypt. Each of these groups has its own geochemical and structural characteristics which make it different from the others. These characteristics are briefly discussed in the following paragraphs.

The conclusion of EL SHAZLY, EL SOKKARY and KHALÍL [1972] that Shaitian granite is the oldest among earlier granites is confirmed later by the work of EL RAMLY and SALLOUM [1973] on the tectonic regioning of the basement rocks of Egypt. The latter authors showed that only Shaitian type plagioclase granites are associated with the so-called median masses, the latter are regarded as the oldest parts of the basement geosyncline. HASHAD *et al.* [1971] assigned an age of 865 m. y. for Shaitian granites which is the oldes among the ages of other Egyptian granites.

The azimuth of the deep seated fault in G. Shait area is N8W which is strikingly the same azimuth for the granite of W. Baba (Sinai), despite of a separating distance of about 500 kms. Moreover, the two granites show together impoverishment in Rb with varying enrichment trends in Sr, i. e. undifferentiated character of granites.

It is worth to notice that trace elements data of the two pebbles from the geosynclinal sediments from Qift-Quseir area show the chemical characteristics of Shaitian

type plagioclase granites. This gives an indication that the latter granites are either older or contemporaneous with the geosynclinal sediments, a matter which again sets them as the oldest granites in Egypt.

On the other hand grey granites are related to geosynclinal structure and not to median masses like the previous group of Shaitian granites. They are typified by the granites of El Sibai area which show deep seated faults with NW—SE trends, and an azimuth of N33W. These granites till show a common geochemical feature with Shaitian granites which is the impoverishment in Rb and enrichment in Sr characteristic for undifferentiated acidic rocks.

In other words, it is possible to distinguish, particularly in the field, between the two groups of earlier granites, the first is the oldest (Shaitian) and emplaced only within the terrains of median masses, while the second group (grey) is comparatively younger and formed as a result of a later tectonic phase within the geosyncline.

To sum up, Shaitian granites are compared with grey granites from the points of view of their chemistry and azimuth of deep seated faults. On the other hand, the two groups are contrasted in a sense that only Shaitian granites are associated with median masses beside that only grey granites show some development of their potash feldspars.

To the first time, it becomes now possible to distinguish, particularly in the field, the two subgroups of younger granites formerly recognized as one group. These two subgroups are the normal pink-red granites (pre- or syn-Hammamat) and the strongly differetiated pink-red members (post-Hammamat). The former show deep seated faults usually with latitudinal trends i. e. EN—WS, while the latter are clearly emplaced on deep seated faults usually with longitudinal trends i. e. NW—SE. Geochemically the normal pink-red granites show great reduction in their Sr content with rising Rb values and almost normal distribution of Ba. On the other side, strongly differentiated granites show a sudden drop in their Ba and Sr contents with varying enrichment trends in Rb.

The trace elements data for the two pink granite pebbles from Hammamat conglomerates are conformable with those of the normal pink-red granites with latitudinal trends of deep seated faults. This assures that the latter granites are somewhat older than the strongly differentiated granites. Thus granites with latitudinal system of faults are either pre- or syn-Hammamat, while those with longitudinal faults are post-Hammamat.

On the basis of available geochronological data, the normal pink-red granites give an age ranging from 621—515 m. y., while the strongly differentiated rocks give an age for one of their varieties as 488 m. y. This difference in age (133 m. y.) between the two groups of younger granites explains the lapse of time usually reported an many works for the time of emplacement of these granites. However, it should be noted that the available geochronological data up till now are far from being stable due to a multitude of reasons. Therefore strong reliability on these data is not guaranteed.

The following granite masses are classified with normal pink-red granites that are characterized in the field and on geologic maps by latitudinal system of faults (EN—WS): G. Kadabora, G. Elba, G. Igla, G Hangalia, G. Abu Diab and G. Siwiqat El Arsha. On the other hand, the following plutonites are classified with strongly differentiated pink-red granites that are characterized by a longitudinal system of deep seated faults (NW—SE): G. El-Sibai, Um Negat, G. El Muelha, W. Um Dubr, G. Abu Tyour, G. Homret Wagat, G. Homret Akaram and G. El Atawi.

The granite masses of the south western desert, namely those occurring in the areas of G. Um Shaghir, G. El Asr, G. Abu Bayan El Bahari, G. Abu Bayan El Qibli, west of G. Abu Bayan El Qibli and Bir Tarfowi, are shown to posses a latitudinal system of deep seated faults. Unfortunately, no reliable trace elements data are available for these granites. But on the basis of the preceeding geotectonical considerations, these granites might belong to the normal pink-red group of Egyptian younger granites.

It is worth to notice that the strongly differentiated pink-red granites which are post-Hammamat are situated along deep seated faults with NW—SE direction. This fault trend is nearly the same like that of earlier granites (Shaitian and grey). Therefore strongly differentiated pink-red granites might be emplaced on rejuvenated fault system originally started by the time of emplacement of old granites. This may tentatively explain why some pink-red granites are seen cutting through or penetrating old grey granites. Admittedly, the activity of the longitudinal deep seated faults during the geotectonic development of the geosynclinal system is more pronounced than that of the latitudinal system.

Anomalous pink granites are a special division of pink-red granites which abnormal distribution of trace elements e. g. unexpected enrichment in Sr or Ba or lowering of Rb values. Their deep seated faults take a different trend from that of the previous two groups i. e. either NE—SW (contrasted with the NW—SE system for strongly differentiated granites) or ES—WN (contrasted with EN—WS for normal granites).

Aswan granites stand in a geochemical province on account of the peculiar distribution of their major and trace elements [El Sokkary, 1970]. As an illustration of this peculiar distribution, the coarse varieties show enrichment trends in Ba and Sr beside Rb. The main set of deep seated faults of Aswan plutonites take a NW—SE direction with azimuth ranging between N10W and N30W. Since this fault trend is the same like that of strongly differentiated pink-red granites, therefore, it is likely that Aswan granites can be classified as belonging to the youngest granites in Egypt. However, differences in chemistry between Aswan granites and the strongly differentiated granites are attributed to the influence of older basic country rocks on the invading Aswan acidic plutonites.

Estimates of the age of these granites are somwehat variable, but the age of 470 m. y. given by El Ramly [1962] is consistent with the present suggession that Aswan plutonites are among the youngest granites in Egypt.

CONCLUSIONS

On geochemical and geotectonical basis, six fundamental groups of granites could be identified in the basement rocks of Egypt. These groups are Shaitian, grey, normal pink-red, strongly differentiated pink-red, anomalous pink and Aswan granites. Shaitian granites are definitely the oldest granites and are associated with the median masses. Grey granites, despite of some similarities in their chemistry with Shaitian granites, are related to geosynclinal system.

It is now possible through the present study to distinguish the pre- or syn-Hammamat pink-red granites from the post-Hammamat members. The former usually show latitudinal trends (EN—WS) of their deep seated faults, while the latter show generally longitudinal trends (NW—SE). Chemically, the former group are normal granites while the latter are their strongly fractioned members.

Anomalous pink granites show unusual distribution of certain trace elements. The trends of their deep seated faults are different from those of the previous two groups of pink-red granites. These trends take the NE—SW or ES—WN direction.

Aswan coarse plutonites stand in a geochemical province. Their main system of deep faults take a NW—SE direction which is the same as that of strongly differentiated (post-Hammamat) pink-red granites. This probably makes Aswan plutonites among the youngest granites in Egypt.

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CONTRIBUTION TO QUANTITATIVE DETERMINATION OF LAYER SILICATES BY CHEMICAL METHOD*

I. VARSÁNYI

INTRODUCTION

The layer silicate minerals of sedimentary basins are of great importance both in theoretical and practical respect. Great attention has been directed to their study in the last decade in consequence of their role in the genesis, migration and exploitation of petroleum.

For the sake of rendering possible the study of distribution and history of evolution of layer silicates in the sedimentary basins, first of all some analytical problems had to be solved. The most general method for the quantitative and qualitative analysis of crystalline layer silicate minerals is the X-ray diffraction analysis. It seems to be, however, advantageous to comparate the data obtained by X-ray diffractometry with results of other methods.

From this point of view attention has to be turned to the chemical method proposed by ALEXIADES and JACKSON [1966] for quantitative determination of clay minerals, amorphous material, quartz and felspar in soils and sediments, respectively.

PRINCIPLES OF THE CHEMICAL METHODS

The method according to ALEXIADES and JACKSON [1966] was developed for quantitative determination of the following minerals: montmorillonite, vermiculite, mica, kaolinite, dickite, chlorite, talk, quartz, feldspar and amorphous material.

The single steps of the method are based on measurements of ion exchange capacity, selective dissolution in NaOH, fusion by sodium pyrosulfate and on determination of ignition loss of samples.

The single steps of this complicated method are comprised in a flow sheet shown in *Fig 1*, constructed on the basis of own experiences.

The preparation means suspending the pulverized core samples in water and their fractionating. A pretreatment has to be made before analysis to remove carbonates, organic matters and iron oxides. This procedure is made with NaOAc solution, $Na_2S_2O_4$ solution and H_2O_2. Then the samples are washed with KCl or NH_4Cl depending on what component is to be determined, to form monocationic K-or NH_4-minerals. Before chlorite determination ions in exchange positions are replaced by K^+ because of the slight hydration of this ion. The determination of mica, quartz and felspar is based on that of the K^+ ion, therefore, they cannot contain any K^+ in exchange positions, thus the saturation is carried out by NH_4^+

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ions. Before vermiculite and montmorillonite determinations samples have to be saturated by Na^+ for it can be exchanged easily and completely by K^+ or Mg^{2+}. At the determination of amorphous material or kaolinite K^+ or NH_4^+ may be used for saturation.

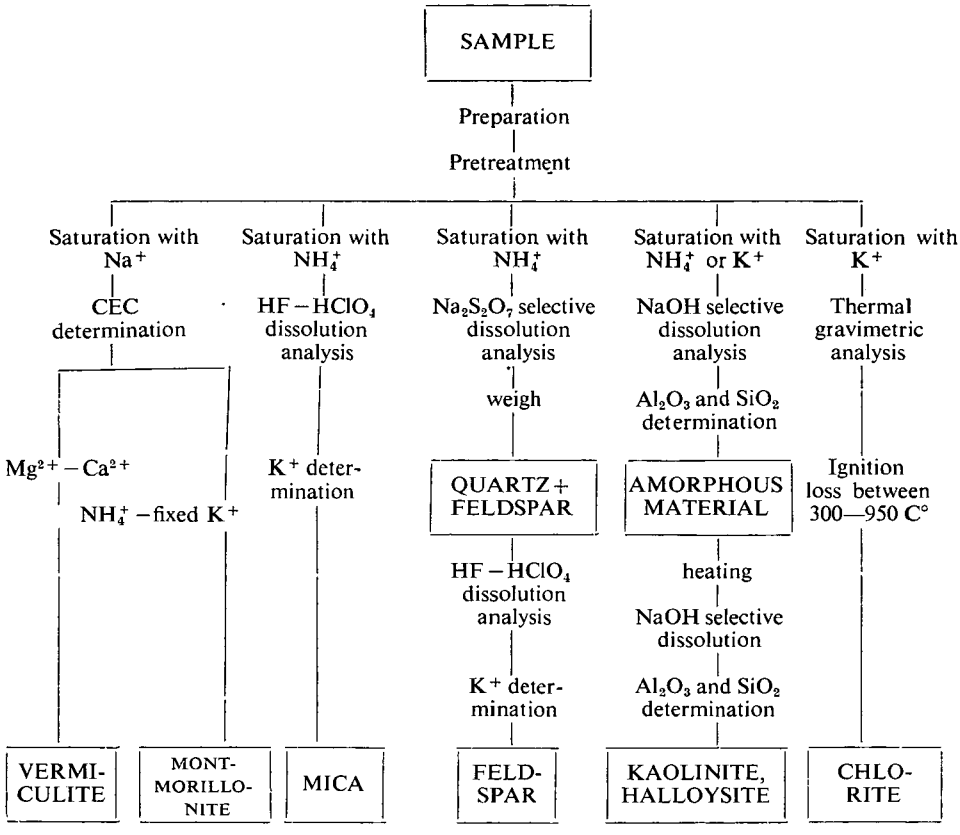

Fig. 1. The steps of the chemical method

Vermiculite determination is based on the high charge density of vermiculite and its K^+ fixing capacity [ALEXIADES and JACKSON, 1965]. The total cation exchange capacity (CEC) of the samples is measured by $Mg^{2+} \rightarrow Ca^{2+}$ ion exchange.

> Ca^{2+} in the $MgCl_2$ solution is determined as follows: dilute 10 ml aliquot to 200 ml, add 20 ml of 6% NaOH solution and 1,5 ml of Eriochromblue SE indicator to it, stir the solution and titrate it with 0,05 M Komplexon III.

After CEC determination by Ca^{2+}, the samples are saturated by K^+ and heated to 110 C° overnight to dehydrate and collapse the layers of vermiculite and to fix K^+. The non-fixed K^+ is replaced by NH_4^+. The concentration of K^+ is measured by flame photometry. The amount of vermiculite can be calculated from the difference of the two CEC measurements taking into account that the interlayer charge of vermiculite amounts to 154 meq/100 g.

Montmorillonite determination is carried out by CEC determination, too. The CEC is measured by $NH_4^+ - K^+$ cation exchange. The CEC of montmorillonite is

105 meq/100 g. The amount of amorphous material has to be considered in the calculation if its SiO_2/Al_2O_3 molar ratio is >3. In this case also the montmorillonite-like components are dissolved in NaOH consequently this part of the sample would be counted as amorphous material and as montmorillonite, too.

The determination of *mica* of sedimentary rocks is based on its K_2O contents. The sample saturated with NH_4^+ is submitted to $HF—HClO_4$ dissolution. After this procedure K^+ is measured by flame photometry. The K_2O contents of generally dioctahedral micas are 10 per cent. The K_2O contents of feldspar are subtracted from the total K_2O of the samples.

The amount of *quartz* and *feldspar* is determined after $Na_2S_2O_7$ fusion. In this way the other, layer silicate minerals are decomposed by removing octahedral cations, so they become soluble in NaOH solution. SO_3 formed during the fusion of $Na_2S_2O_7$ means an acid treatment for the layer silicate minerals at high temperature and makes them soluble.

The weight of the insoluble residue gives the amount of quartz together with feldspar. The K^+ contents of the residue are measured after having dissolved it in $HF—HClO_4$.

During fusion by $Na_2S_2O_7$ there is an ion exchange, K^+ in feldspar is replaced by Na^+ from $Na_2S_2O_7$. Boiling in 0,5 n NaOH solution results some loss in the amount of quartz and feldspar. Both effects depend on the grain size. The losses coming from these effects have to be corrected by a factor (KIELY and JACKSON, 1965]. The grain size influences the value of the correction factor. The calculation is based on the 16,9 per cent K_2O content of feldspar.

There is no ion exchange if the fusion is carried out by $K_2S_2O_7$. In this case the K^+-excess can falsify the results of the determination. Another problem in connection with $K_2S_2O_7$ is that the solubility of the K-silicate minerals, formed during the fusion, is less than that of the Na-silicates.

The determination of *amorphous material* and *kaolinite* is based on dissolving monocationic (K or NH_4) minerals in NaOH solution after a short boiling (2,5 min). Amorphous material dissolves while the crystalline phase is not damaged.

Si and Al concentrations are measured in NaOH solution. Calculating the amount of amorphous material and kaolinite contents the SiO_2 and Al_2O_3 and water contents are taken into consideration.

Si determination was made according to RAINWATER and THATCHER [1960] with some modifications because the determination in this case was carried out in NaOH solution. Si determination:

> Pipet 4 ml aliquot of sample into 50 ml volumetric flask. Add 15 ml of 0,6 n HCl and 5 ml of 5 per cent NH_4 molybdate. Let it stand for 5 minutes, then add 5 ml of 17 per cent Na_2SO_3, mix, dilute to volume and let it stand for 30 minutes before measuring. Measuring was made with a "Spektromom 360" spectrophotometer at 700 nm wavelength. When calibration curve was determined only 10 ml of 0,6 n HCl was added.

The Al determination was carried out according to SNELL and SNELL [1951].

> Transfer 10 ml aliquot of sample to a 50 ml volumetric flask. Adjust the acidity to 0,7 ml concentrated hydrochloric acid. Dilute to about 30 ml and add 5 ml of 0,1 per cent Alizarin S solution. Add 2 ml of 1:2 ammonium hidroxide and mix. Let it stand for 10 minutes and add 10 ml of 1:2 acetic acid. Mix, dilute to volume and let stand for 20 minutes before measuring. Measuring was made with a "Spektromom 360" spectrophotometer at 490 nm wavelength.

Kaolinite is determined as amorphous material because the crystal structure of kaolinite is destroyed at 525 C° and so it becomes soluble in NaOH solution. The calculation of kaolinite contents depend on the SiO_2/Al_2O_3 molar ratio.

The SiO_2/Al_2O_3 molar ratio $\lesssim 2$ indicates free alumina or dissolved interlayer aluminium. In this case only the SiO_2 contents are considered. Kaolinite has 46,5 per cent SiO_2 contents in average.

When SiO_2/Al_2O_3 molar ratio is >3, 2:1 layer silicate minerals were dissolved. The kaolinite contents are calculated on the basis of Al_2O_3. The theoretical Al_2O_3 contents are 39,5 per cent in kaolinite.

When SiO_2/Al_2O_3 is between 2 and 3 the calculation is on the basis of average of SiO_2 and Al_2O_3 contents.

The *dickite* can be determined in the same way. The dickite becomes amorphous at 625 C°.

Chlorite is determined by thermal gravimetric method [ALEXIADES and JACKSON 1967]. K^+-saturated samples are used for hydration of K^+ ion is minimum. The chlorite contents are calculated on the basis of the total ignition loss (OH water) of the samples between 300 °C and 950 °C. The water allocated to the minerals present other than chlorite, is subtracted from the total ignition loss. A correction is applied for the weight gain of FeO present and oxidized by heating to 950 C°. A 14 per cent OH water is attributed to the chlorite.

FeO determination: 0,3 g sample is dissolved in H_2SO_4—HF under CO_2 atmosphere, for 10 minutes, at 130 C°, in Pt crucible. Then it is put into 100 ml saturated boric acid and titrated with 0,01 N $KMnO_4$ solution.

REMARKS IN CONNECTION WITH DATA OBTAINED BY CHEMICAL METHODS

After obtaining experiences on the applicability of the method outlined above using relatively well identified layer silicates and other minerals, respectively, core samples from Makó-trench were analyzed. The amount of layer silicate minerals, quartz and felspar were determined by the chemical method and X-ray diffractometry. The samples were ground in a ball mill, so that grain size should be under 60 μm. The time of grinding was short to avoid destroying crystal structure of clay minerals [JUHÁSZ, 1969].

The powdered samples were then suspended and the fractions of grain size $\leqq 20\,\mu m$ were separated. Experiments were carried out with these fractions.

The composition of 17 core samples from Makó-1 borehole is shown in Table 1.

Some problems, however, arose during the experiments. and calculations.

When vermiculite is determined its CEC is calculated as the difference of two CEC values measured in two different ways, but the CEC numerical value depends on the way of determination, namely what kind of ions are used for saturation.

The total CEC of the samples is determined by $Mg^{2+} \rightarrow Ca^{2+}$ ion exchange. The non-fixed K^+ is replaced by NH_4^+. The latter ion exchange means the CEC of the other than vermiculite minerals. These two CEC-s are not commensurable, so their difference must not be considered as the CEC of vermiculite.

The 10 percent K_2O contents for mica given in the literature may be questionable because only muscovite has 10 per cent K_2O. The K_2O contents of illite are smaller than that of the muscovite [HOWER and MOWATT, 1966]. Illite does not form discrete phases in many places, but it is rather a mixed-layer illite-montmorillonite. Illite is considered as an end member of the illite-montmorillonite series [HOWER and MOWATT, 1966].

TABLE I

Minerals present in the core samples from Makó-1 borehole

	Quartz	Albite	K-feldspar	Amorphous material	Kaolinite	Chlorite	Mica—Illite	Montmorillonite	Vermiculite	Total
I	19,6	2,3	1,0	7,7	4,6	11,7	22,1	24,1	0,0	96,1
II	18,0	3,6	0,8	7,3	0,0	18,3	26,9	15,8	0,0	88,7
III	10,1	2,1	0,5	9,6	4,9	12,7	27,3	21,1	0,0	88,3
IV	22,0	3,6	1,5	5,2	5,4	11,8	25,5	20,7	0,0	95,8
V	20,6	1,9	0,9	5,9	3,5	18,4	24,5	12,5	0,0	88,2
VI	21,0	1,9	1,1	3,7	18,8	3,3	24,3	13,8	0,0	87,9
VII	19,6	4,9	1,2	9,8	1,7	22,8	25,6	0,0	0,0	85,6
VIII	13,8	5,3	2,2	4,5	2,9	20,1	28,6	14,2	0,0	91,6
IX	16,8	3,1	1,8	2,7	0,9	20,7	26,2	15,2	2,5	87,4
X	20,2	4,0	1,3	2,6	0,0	27,8	25,3	16,3	0,0	97,5
XI	11,5	3,9	1,1	4,7	0,0	29,9	27,6	8,1	0,0	86,5
XII	17,4	4,4	0,6	4,6	1,9	21,6	26,9	5,8	0,0	82,2
XIII	19,6	3,2	0,8	16,2	0,0	25,4	26,4	1,0	0,0	82,4
XIV	19,4	3,8	0,4	9,1	0,0	17,8	28,8	8,9	0,0	89,1
XV	13,5	2,3	0,2	0,6	0,0	22,0	26,2	19,0	2,6	83,3
XVI	23,0	6,8	1,3	1,2	0,3	24,4	28,2	10,2	0,0	95,4
XVII	16,9	3,7	0,4	0,5	0,0	24,4	31,6	11,1	0,0	88,6

TABLE 2

SiO_2/Al_2O_3 molar ratio of the amorphous material and quartz contents in the pulverized non fractionated samples

	I	II	III	IV	V	VI
SiO_2/Al_2O_3	8,2	8,6	13,0	19,0	11,4	20,9
Quartz	20,6	23,9	38,1	39,7	50,6	42,9

These samples come from the Makó-2 borehole.

According to the previous fact the mica contents in core samples containing not only muscovite but illite and mixed-layer illite-montmorillonite cannot be calculated on the basis of 10 per cent K_2O contents.

Calculating the feldspar contents, different factors are taken into consideration for the fractions of different size. The samples analyzed contained particles in every size below 20 μm. Instead of complete grain size analysis we determined correction factors using a felspar standard of grain size $\leqq 20$ μm. The loss coming partly from $Na^+ \rightarrow K^+$ ion exchange, partly from the solubility of feldspar was corrected by these factors.

Considering the ion exchange, both K^+ and Na^+ contents of feldspars were measured and calculated, respectively. The Na_2O content measured after $Na_2S_2O_7$ fusion and the data of X-ray diffractometry suggested the presence of albite not only that of microcline as it was in the paper referred [KIELY and JACKSON, 1964]. So we calculated with 16,9 per cent K_2O contents for K felspar [KIELY and JACKSON, 1964]

TABLE 3

SiO_2/Al_2O_3 molar ratio of the amorphous material and quartz contents in the $\leqq 20$ μm size fraction

	SiO_2/Al_2O_3	Quartz
I	4,5	19,6
II	5,8	18,0
III	8,4	10,1
IV	6,5	22,0
V	8,5	20,6
VI	2,7	21,0
VII	9,6	19,6
VIII	5,2	13,8
IX	2,1	16,8
X	1,5	20,2
XI	3,8	11,5
XII	6,6	17,4
XIII	22,4	19,6
XIV	4,7	19,4
XV	0,4	13,5
XVI	1,2	23,0

and 10,7 per cent Na_2O and 1,0 per cent K_2O for albite was taken into account as mean values of data of albite analyses comprised in a handbook by HINTZE [1893].

The reliability of the determination of amorphous material was proved by a pure kaolinite sample. The sample heated to 600 °C became amorphous tested by X-ray measurements and it dissolved completely in NaOH solution.

The fine grain size fraction of samples has large quantities of amorphous material. It is difficult to say whether the observed great quantity of amorphous material is due enrichment is caused by the partial damage of the crystal structure of layer silicates during the preparation.

The data obtained by chemical method differ from those by X-ray diffractometry. It can be attributed to the presence of much amorphous material.

To obtain data comparable with that of the X-ray diffractometry the chemical analyses were carried out in pulverized non fractionated samples from Makó-2 borehole. The data obtained in two different ways coincided well. The amount of amorphous material was less than it was in the $\leqq 20\,\mu m$ size fraction of fractionated samples.

In spite of this the pulverized and non fractionated samples are not suitable for chemical analysis because of their badly defined grain size. The value of CEC and the calculation of feldspar depend on the grain size. Another problem is that these samples contain quartz in large quantities and the SiO_2 contents can dissolve in NaOH solution, as it is shown in Table 2.

The same data of the $\leqq 10\,\mu m$ size fraction of the samples from Makó-1 borehole are denoted in Table 3.

It seems that the adaption of the chemical method is more suitable in clay fraction of samples than in the average samples without separating their clay fraction.

CONCLUSIONS

Comparing the X-ray diffraction and chemical data concerning the determination of the mineral composition of sedimentary rock samples. it seems that both methods have advantages and disadvantages. The joint adaption of the two methods means a good possibility of the determination of clay minerals, amorphous material, quartz and feldspar. For example, the determination of amorphous material can be carried out quickly and exactly by chemical methods but X-ray diffractometry is not suitable for it. The question whether samples contain discrete phases of illite, montmorillonite, vermiculite and chlorite or mixed layer structures of them, can be answered only by X-ray diffractometry. The latter method is faster than the chemical method, but the advantage of the chemical method is that constituents can be determined in very small quantities, too.

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CONTRIBUTIONS TO THE INTERPRETATION OF SOLUBLE ORGANIC MATERIALS OF SEDIMENTARY ROCKS**

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INTRODUCTION

The study of the types and pecularities of the insoluble organic material as well as that of the organic material soluble in organic solvents plays an important role in geochemical investigations in connection with hydrocarbon prospection.

The investigation of the soluble organic material, the determination of the ratio of the quantity of the soluble and insoluble organic material is closely connected with the problem of migration, with differentiation between the primary and secondary character of the soluble organic material. In the relating literature one can find a diversity of opinions.

Still less the study of the insoluble dispersed organic material in the sedimentary rocks, the determination of its character, type, grade of diagenesis as well as of its reduction capacity has a paramount importance. The determination of the parameters mentioned theoretically renders possible to draw essential conclusions concerning the role of the insoluble organic matter in question in the generation of hydrocarbons. In the related literature, however, very controversary ideas may be found. One of them over-emphasizes perhaps the importance of the source rock concept though there is no method rendering possible the distinct and unequivocal determination of the source rock character of the beds whereas according to other opinions, represented by COLOMBO and others, under special conditions any sedimentary bed can contribute to a smaller or greater extent to the generation of hydrocarbons which can accumulate in the reservoir rocks.

In the present paper it is not an aim to give a critical evaluation of the related literature rather some ideas and questions, respectively, will be raised sometimes increasing only the number of question open so far, however, such questions may also contribute to the solution of the problems.

The sedimentary rock samples investigated are originated from the Upper Pannonian, Lower Pannonian and Miocene layers of the south part of the Great Hungarian Plain.

The investigations were carried out on behalf of the Hungarian National Oil and Gas Trust.

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QUESTIONS CONCERNING THE INTERPRETATION OF THE SOLUBLE ORGANIC MATERIAL CONTENT

The Bitumen A content of the samples was extracted by chloroform in a SOXHLET apparatus, and after having removed the solvent, the amount of Bitumen A was weighed. The extraction thereafter was continued with benzene: acetone: methanol (70:15:15). After exhaustive extraction and removing the solvent the amount of the extract (BAM extract $\approx$ Bitumen C) was weighed.

The total organic carbon content of the samples was determined by ignition on oxygen stream. From these values the bitumen coefficient was calculated using the formula

$$\frac{\text{Bitumen A} \cdot 100}{C_{org}}$$

The lowest, the mean and the highest values of data mentioned above are comprised in Table 1 denoting also the depth interval of the single borings wherefrom the samples were originated.

In Table 2, however, the samples are grouped according to their age and the mean values of data related to the samples of the same age are shown.

It is to be noted that of the samples of borings Fe-3—13 three showed a fairly extreme chloroform bitumen concentration. One sample was taken from the Upper Pannonian (Bitumen A=0.1928%) and the other two were from the Lower Pannonian layers (Bitumen A amounts to 0.5488% and 0.5730%, respectively). The samples are medium-grained and fine grained sandstones.

As it is seen the elimination of the samples with higher Bitumen A content at the calculation of the mean values influences only the calculation of the mean value

TABLE I

The lowest, mean and highest values of some parameters measured in the samples investigated grouped by the borings

№ of borings	Number of samples	Depth m	Bitumen A %	BAM extr. %	C_{org} %	Bitumen coeff.
M-2	31	2000—4800	0.0079	0.0051	0.05	2.93
			0.0360	0.0228	0.28	14.62
			0.0660	0.0563	0.68	34.60
Fe-K-1	9	1450—2060	0.0099	0.0120	0.12	2.91
			0.0274	0.0304	0.42	8.41
			0.0530	0.0533	1.20	24.75
Fe-3-13	21	1700—2450	0.0221	0.0170	0.03	5.32
			0.0951	0.0352	0.30	43,77
			(0.0380*)	(0.0336*)		(27.59*)
			0.5730	0.0868	0.93	177.00

* mean values without taking into account three extreme values

of the Bitumen A concentration, however, at the calculation of the mean value of the BAM extract it causes only very slight differences. It seems that in the three samples mentioned the fairly considerable increase of the chloroform bitumen compared to its mean value is not accompanied by the increase of the amount of the BAM extract, even in two samples the value of the latter is lower than that of the other samples from the same area.

The highest mean value both for the Bitumen A and BAM extracts and therefore for the total soluble organic material could be stated in samples of borings Fe-3—13, however, the mean concentration of the BAM extract remained always below that of the chloroform bitumen. In the samples of boring M-2 the mean value of the BAM extract is lower than that of the chloroform bitumen, however, both values are lower than measured in the samples of borings Fe-3—13. In the samples of boring Fe—K—1 an inverse relation could be established, the mean BAM extract concentration exceeds that of the chloroform bitumen and of the borings the samples of Fe—K—1 show the relatively highest mean organic carbon content and the lowest bitumen coefficient.

Considering the ratio of the amounts of chloroform bitumen and BAM extract, respectively, of the samples taken from the three area mentioned it seems to be advantageous to consider TISSOT's [1969, 1971] order of ideas and statements. According to him the amount of organic compounds of higher molecular weight containing also many hetero-atoms decreases by the depth owing to formation of lighter compounds without or poor in hetero-atoms.

According to TISSOT during the hydrocarbon generation first the formation of the heavier compounds with hetero-atoms takes place from the kerogen. These compounds would correspond to the compounds of the BAM extract and the formation of the lighter components (chloroform bitumen) will take place on account of them.

The mechanism assumed was also experimentally proved. The samples of Toarcian sediments of the Parisian Basin were extracted by chloroform, thus in the samples merely the BAM components and the kerogen remained. Heating the samples under temperature and pressure corresponding to the conditions established in the sedimentary basin investigated, formation of chloroform bitumen could be stated preceding a shortlived formation of a new amount of BAM components. Thus, the compounds of the BAM extract would represent an important step of evolution between the kerogen and the components of the petroleum.

Starting from the concept outlined above the question would arise what connections may be observed among the chloroform bitumen, the BAM extract and the total organic carbon content in the samples of sedimentary rocks from the south part of the Great Hungarian Plain.

The connections according to TISSOT can hardly be stated on the basis of the data of Table 1, however, the decrease of the amount of the BAM extract by the depth is faintly observable in the section of single borings. It is to mention that the knowledge of the ratio of the single fractions of the BAM extract and their change by the depth, respectively, would have given rather meaningful informations.

Grouping, however, the data according to the depth of burial i. e. according to the age of the samples and the mean values of the parameters mentioned are calculated for the Upper Pannonian, Lower Pannonian and Miocene samples, some connections can be established.

Investigating the mean values of parameters by grouping the samples according to their stage and epoch, respectively, it may be stated that the amount of the BAM extract, as well as, the C_{org} decreases from the Upper Pannonian to the older Miocene

TABLE 2

Mean values of chloroform bitumen, BAM extract, organic carbon content as well as the bitumen coefficient of the samples in function of their stage

Stage Epoch	Number of samples	Bitumen A %	BAM extr. %	C_{org} %	Bitumen coeff.
Upper Pannonian	15	0.0417 0.0309*	0.0413 0.0391*	0.36 0.37*	14.08 9.50*
Lower Pannonian	36	0.0607 0.0390**	0.0314 0.0316**	0.315 0.313**	25.37 19.55**
Miocene	10	0.0272	0.0189	0.28	12.56

*, ** mean values without one and two extreme values

i. e. by the depth, moreover, this connection between the change of the amount of the BAM extract and the organic carbon is nearly linear as shown in *Fig. 1.*

Naturally, the change shown in *Fig. 1* is not a monotonous one bed by bed, rather a tendency obtained by grouping and averaging the samples according to their ages can be stated.

The chloroform bitumen content of the samples does not show similar connections with the total C_{org} and the depth, respectively. Its mean value in the samples of Upper Pannonian practically is nearly the same as the mean of the amount of the BAM extract, in the samples of the Lower Pannonian its mean value exceeds that of the BAM extract (to a fairly great extent taking into account the samples with extreme chloroform bitumen content, too) and in the Miocene samples also exceeds slightly the mean value of the BAM extract.

Leaving the three samples with extreme chloroform bitumen content out of consideration, it gives merely negligible differences in the calculation of the mean value of the BAM extract and the total C_{org}, however, in the case of chloroform bitumen, especially in samples from Lower Pannonian, more considerable differences can be established (Table 2).

As shown in *Fig. 1,* besides a nearly linear correlation between the mean values of the BAM extract and C_{org} also the decrease of the amount of these constituents by depth is accompained by increasing temperature measured in the M—2 borehole.

BRENNEMAN and SMITH (1958) in their paper cited by NAGY and COLOMBO [1967] stated that between the crude oil and the organic extract of its alleged source rocks no unique property could be observed which would be considered as a linkage between crude oil — source rock pairs.

In connection with this statement taking into consideration the correlation shown in Table 2 and *Fig. 1,* respectively, perhaps it may be concluded that within the beds there exists presumably a genetically closer connection between the insoluble organic matter and the compounds of the BAM extract with higher molecular weight than between the insoluble organic material and the chloroform bitumen extractable from the same samples. The lighter components of the chloroform bitumen have a greater migration ability than the heavier compounds of the BAM extract, with higher molecular weight. Thus, a greater or smaller portion of the chloroform bitu-

men in the different beds can be taken as migrated there and so this portion has really no genetic connection with the insoluble organic material of the bed in question. On the other hand, it may be assumed that rather the heavier compounds of the BAM extract formed from the insoluble organic material remained — at least a portion of them which did not turned into lighter compounds — in the bed where they formed, together with the rest of the insoluble organic material.

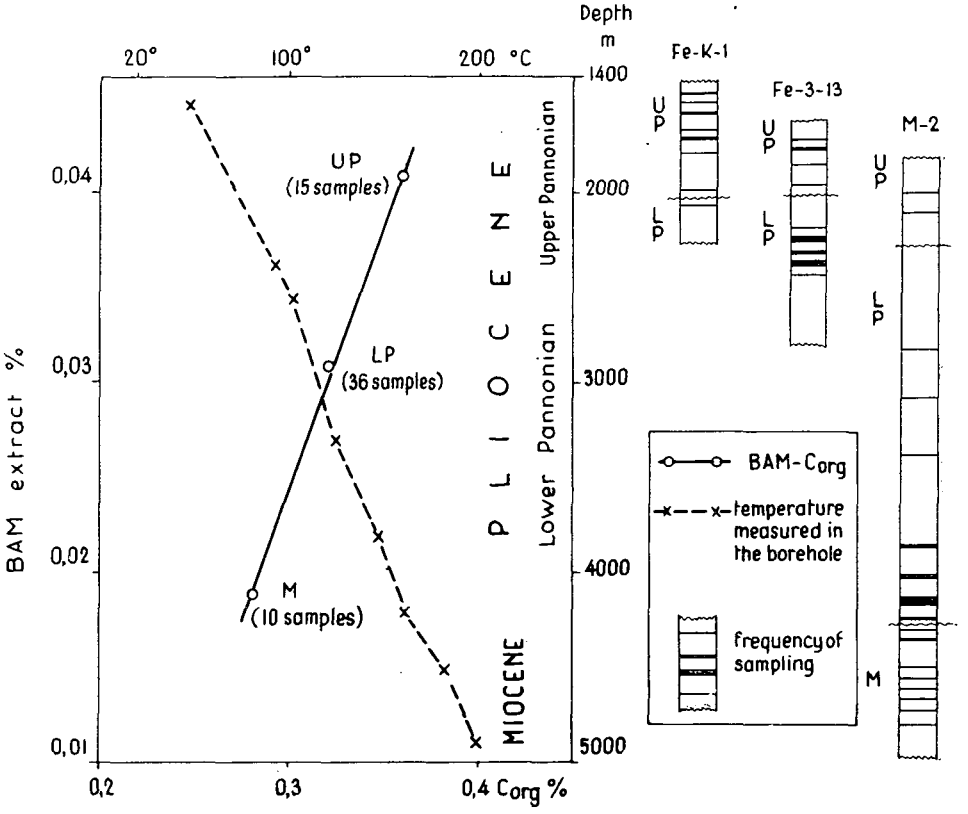

Fig. 1. Connection of mean values of the BAM extract and organic carbon grouping the samples and averaging the values according to the age (depth) of the samples investigated

According to PHILIPPI [1957[cited by NAGY and COLOMBO [1967] the source quality of sediments would be estimated by the amount of residual hydrocarbons generated per unit weight of dry rock. Merely it is very difficult to prove that the "residual" hydrocarbon is really indigenous to the bed investigated and not migrate there after the sedimentation.

In the literature many references, statements concerning the differentiation of primary and secondary bitumen can be found. One of the parameters for delimitation of primary and secondary bitumen is the so-called bitumen coefficient. It renders, however, only qualitatively probable whether primary or secondary bitumen is in question but the distinct delimitation of the two depends on many local factors as was explained by SIMANEK [1968].

It seems that many open questions still exist and will remain in connection with the bitumen coefficient especially with its interpretation. Some authors calculate with the formula $\frac{\text{Bitumen A} \cdot 100}{C_{org}}$ others calculate instead of C_{org} with the organic material in the denominator. The amount of the organic material is calculated from the C_{org} content determined by ignition in oxygen stream and multiplying this value with an "organic factor". But what may be taken as a correct „organic factor". Factor 1.33 was used by VYCEV and MATEEVA [1968] for recalculation of C_{org} into the organic material, in other papers different factors can be found depending on the age and rank of coalification. The factor is 1.22 in the case of metamorphic shales and 1.75 in the case of recent sediments. It seems that it is more adventageous to use in the denominator the C_{org} per cent if on the basis of detailed C—H-analysis of isolated organic material the organic factor suitable for real calculation is not known.

A further problem mentioned also in PHILIPPI'S paper referred to what bitumen coefficient can be assumed as dividing value between primary and secondary bitumen. According to RODIONOVA (cited by LEGMANN *et al.*) the border is at 5 in the case of terrigenous rocks and 15 in that of carbonate rocks. According to other authors (LEHMANN *et al.*, 1968] in the case of very low organic material content it is more adventageous to use the diagram constructed by WASSOJEVITCH. Using this diagram it renders the presence of primary bitumen probable also at lower C_{org} content (below 0.6%) and relatively higher bitumen coefficient. At such values using the delimitation according to RODIONOVA the bitumen might be considered as secondary. It seems that the problem propounded by PHILIPPI has not yet reached a reassuring solution.

Further, if the bitumen coefficient is the expression of the degree of transformation of the insoluble organic material into hydrocarbons, the question may arise, why merely the chloroform bitumen content is taken into consideration although the amount of the BAM extract is also not negligible containing sometimes considerable amount sof paraffine-hydrocarbon fraction, too. Would not be more convenient to take into consideration the paraffine-hydrocarbon fractions both of the chloroform bitumen and the BAM extract.

In the lack of sufficient data an exact delimitation of the primary and secondary bitumen in the samples of the area investigated cannot be given, however, the experiences so far are stimulating on putting up some ideas.

Of the samples investigated those from the Lower Pannonian beds have the highest chloroform bitumen content in average and they showed the highest bitumen coefficient, too. Grouping the data according to the boreholes, the highest mean values for chloroform bitumen and bitumen coefficient were determined in the samples of the boreholes Fe-3—13.

In 58 per cent of the samples of borehole M-2 the bitumen coefficient is lower than 15, in samples of borehole Fe-K—1 88 per cent of the samples whereas of the samples of boreholes Fe-3—13 47.5 per cent has a bitumen coefficient below 15. At the same time in 43 per cent of the samples from the latter boreholes rather high bitumen coefficient values — above 40 — can be found not shown by the samples from the other boreholes.

Grouping the samples from the boreholes Fe-3—13 according to their lithological character into groups of sandstones and marls, claymarls, respectively, and calculating the average values for the different parameters, the data of Table 3 are obtained.

The sandstones corresponding to their resevoir capacity contain considerably more chloroform bitumen than the marls and claymarls, however, at the same time hardly any differences can be found between the amounts of the BAM extract determined both in sandstones and marls, claymarls and between chloroform bitumen and BAM extract content of claymarls, marls. The former idea is coming up again, the components of the BAM extract of at least a portion of them may be in a closer genetic connection with the insoluble organic material present and may be rather considered of primary character. On the contrary, a considerable part of the chloroform bitumen would be perhaps primary in the marls, claymarls and it is dominantly secondary in the sandstones.

TABLE 3

Mean values of chloroform bitumen, BAM extract, C_{org} content and bitumen coefficient in the sandstones and marls, claymarls from boreholes Fe-3-13

	Sandstone	Marl, claymarl
Chloroform bitumen	0.1588	0.0312
BAM extract	0.0336	0.0372
C_{org}	0.25	0.36
Bitumen coefficient	85.55	10.29

The fact that in the migration first of all the componenst corresponding to the chloroform bitumen and within it first the lighter compounds participate is supported also by data of Table 4, showing the ratio of different fractions of chloroform bitumen and the BAM extract of some samples from the boreholes. Fe-3—13.

TABLE 4

Ratio of fractions of chloroform bitumen and BAM extract of samples from boreholes Fe-3-13

Fraction (solvent)	Chloroform bitumen	Chloroform bitumen of extreme value	BAM extract
I (n-hexane)	41—58	80—90	8—28
II (benzene)	16—26	5—7	11—40
III (benzene-ethanol)	23—41	3—9	32—74

(Fraction I contains mainly the paraffine-hydrocarbons, fraction II mostly the aromatic compounds, fraction III contains the so-called acidic resins)

As it can be seen among the fractions of the chloroform bitumen extracted from three sandstone samples having a very high chloroform bitumen content, and therefore considering undoubtedly this bitumen as secondary by migration into these reservoir rocks, fraction I is predominant and the amount of the other two fractions is very low. In the other samples where fraction I is high but not so dominant, the proportion of the other two fractions is also more considerable. Among the fractions of the BAM extract from the same samples the lowest is the proportion of fraction

I and fraction II containing aromatic compounds and even more fraction III corresponding to the acidic resins plays a dominant role.

It may be assumed on the basis of the facts and ideas outlined above that at the delimitation of primary and secondary bitumen more importance should be attributed to the BAM extract besides the chloroform bitumen as well as to the comparison of their fractions separated by column chromatography.

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PROBLEMS IN X-RAY DIFFRACTION DETERMINATION OF MINERAL COMPOSITION OF SEDIMENTARY ROCKS*

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ABSTRACT

Quantitative determination of the mineral composition of core samples originating from deep-bores of the South Great Plain was performed by means of X-ray diffractometry. The difficulties occurring at the determination of muscovite, illite, illite/montmorillonite and chlorite were investigated. The change in mineral composition in the fraction less than 10 microns as compared to the average sample was investigated separately.

It was stated that there is a correlation between the quantities of FeO and chlorite of the investigated samples. A definite relationship can be determined between the amount of chlorite and that of B, V, Ni and Cr. Positive correlation can be determined between the ppm values of Sr and the carbonate minerals.

In the samples of 10 microns the quantity of calcite increased at the expense of dolomite, while dolomite is mostly absent in the fraction of 10 microns.

In the core samples of the "Makó depression trench" albite and acidic plagioclase were found only in the Lower Pannonian strata, in the Upper Miocene formations only albite occurs in determinable quantity. On the basis of the diffractograms the potash-feldspars are absent, under microscope their quantity is subordinate.

INTRODUCTION

In sedimentary sequences the presence of clay minerals is determined on the one hand by the mineral composition of the erosion area, and by transformation resp. neo-formation, i. e. by the diagenetic and epigenetic mineral formation, on the other. Thus, in the sediments such minerals will be found which had undergone certain weathering in the course of fragmentation, transportation and sedimentation. Further, minerals will occur which show certain features of diagenesis, i. e. regarding the structure of the minerals transported into the sedimentary basin it was not in equilibrium with the new pressure and temperature conditions; during the diagenesis such structures were developed which reflected the new conditions.

In the South Great Plain the basement is covered by consolidated sediments of several hundreds, locally of several thousands metres thickness. The material of this huge sediment mass are aleurite, aleurolite, sandstone, marl, lime-marl, occasionally conglomerate. The mineral substance of these formations is partly the fragmented detritus of the erosion area, partly the product of degradation, resp., aggradation followed during diagenesis. The clay minerals or in a general sense the phyllosilicates are of special importance both from the petroleum-geological and from the geochemical point of view.

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EXPERIMENTAL PART

Preparation of the samples for examination

Two kinds of preparation of the samples were used. In the first case the average sample was investigated from which chemical, geochemical, derivatographic, etc. analyses were produced. In this case the grinding of a greater quantity was taken in a ball mill, consequently the material became relatively homogeneous though certain increase of the amorphous phase should have taken into consideration. In the other case the original, non-powdered rock was treated with H_2O_2. In this way material has fragmented into the natural grain size. This treatment caused only a slight chemical change in the minerals, the original grain size, however, remained and became measurable, further the quantitative and qualitative changes of the single fractions could be performed. The suspension obtained in this way was washed out with ion-free water until it became neutral and without using stabilizator the grains less than 10 microns were separated.

Suspension of same concentration was prepared from each material for X-ray diffractometric investigations. The substance was deposited onto the sample holder from the suspension, the deposition time was the same in case of every samples. In this way a film-like oriented preparation was obtained in which the base reflexions of phyllosilicates proved to be exactly measurable. When having performed the X-ray records every samples were held under an atmosphere of ethylen-glycol, during two hours and at 60 °C. Then a new record was done to investigate the expanding layers.

Possibilities and results of quantitative determination of the minerals in several deep-bores of the Great Plain

In these formations in addition to illite (illite-montmorillonite mixed structure), chlorite, muscovite, biotite, quartz, feldspar, calcite and dolomite other minerals occurred only in subordinate quantity (which rarely surpassed one per cent), thus their quantitative and qualitative determinations were neglected.

The routine-like quantitative determination of clay minerals and of the phyllosilicates in general has not developed yet which is due to the wide range of isomorphic replacement possibilities, to polytypics of these minerals and in many cases the uncertainty of the structure, etc. In the sedimentary rocks, such as the material of the deep-bores of the Great Plain, theoretically all the minerals may occur which appear in the erosion area or which got the basin through manifold redeposition. Only a few of them occurs, however, regionally and in greater quantities. The number of predominating minerals is small in these sediments, as well.

One of the most frequent minerals is muscovite-illite. The term illite-hydromuscovite-hydromica is not used in a uniform sense. MAREL, H. W. [1950] and NEMECZ, E. [1973] gives review on the uncertainty and abundance of the terms.

NEMECZ, E. and VARJU, GY. [1970] demonstrated that the position occupation and charge distribution of the illite component of the illite/montmorillonite minerals is continouus towards muscovite. In the illite/montmorillonite of sedimentary origin the Fe and Mg content is higher than in that of hydrothermal origin, further, in the illite/montmorillonite of sedimentary origin the interbedded swelling layer may reach 60 per cent. As to their statement the formation process is probably influenced by the K^+-concentration, in case of higher pH value illite layers are formed. When the pH value decreases, the Al-quantity replacing the Si in the tetrahedral layers also decreases due to the co-ordination change of Al^{IV}/Al^{VI} and swelling layers will

be interbedded. Thus the following minerals can be distinguished in the range: muscovite — hydromuscovite — illite — illite/montmorillonite — montmorillonite.

In the X-ray diffractograms it is troublesome to separate illite and muscovite. This is increased also by the fact that the most intense peaks of these minerals coincide or nearly cover each other and the 3.344 Å peak of the quartz. When the records were made using 2°/minute goniometric angular speed the fact can be only observed that in presence of illite of greater quantity the 3.344 Å peak of the quartz becomes assymmetric towards the smaller angle range, in case of muscovite of greater quantity, however, towards the greater angle range; rarely the two peaks are separated *(Fig. 1)*.

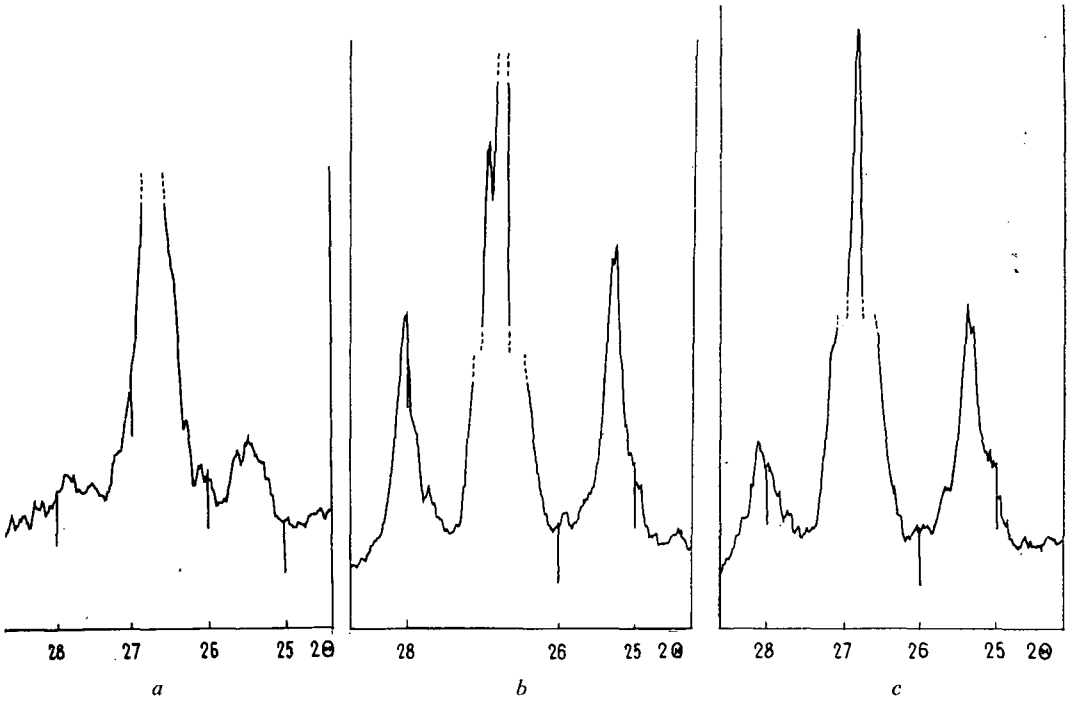

Fig. 1. Asymmetry at the quartz peak of 3.344 Å caused by illite *(a)* and muscovite *(b)*; separated muscovite — quartz peak *(c)*

The polytypics of illite and of the micas in general is well-known. In these formations muscovite is of 2M, illite is of 1M, occasionally 1Md variety. The 001 resp. 002 base reflexion, however, is characteristic of every variety at around 10 Å.

In case of illite and muscovite when investigating the shape and position of the base reflexions 001 (002), the the *d*-value varied between 9.30 and 9.90 Å in case of predominating muscovite. This resulted in a sharp reflexion of small angle breadth and the intercalations between 11.0 and 12.5 Å were usually absent *(Fig. 2)*. When illite — illite/montmorillonite predominated in the sample, however, the peak of the reflexion of about 10 Å is of greater angle breadth and became asymmetric towards the smaller angle range, the reflexions between about 11.0 and 12.5 Å have appeared (as a result of intercalation, *Fig. 3*). The researches of KUBLER, B. [1966] and LAPHAM, D. M., JARON, M. G. [1964] related also to such a phenomenon.

The quality of the intercalated layers should also be taken into account in case of illites. Concerning this problem LUCAS, J. *et al.* [1959] have made investigations. They distingushied three types of the intercalated minerals. The most frequently intercalated layers are:

montmorillonite-type	d_{001}	14 Å (possibly 12 Å)
chlorite	d_{001}	14 Å
vermiculite	d_{001}	14 Å

When illite is the base mineral, on the basis of the investigations performed till now the following possibilities can be expected in the sediments of the Great Plain:

In case of illite/montmorillonite$_{14}$ the position of the peak will be at around 12 Å (in case of montmorillonite$_{12}$ at around 11 Å), the peaks of illite remain unchanged. In case of treatment with ethylene glycol or glycerine the layer of about 14 Å will swell, the peak will be displaced to 15 to 16 Å, and the peak of about 8,85 Å of the montmorillonite will occasionally appear.

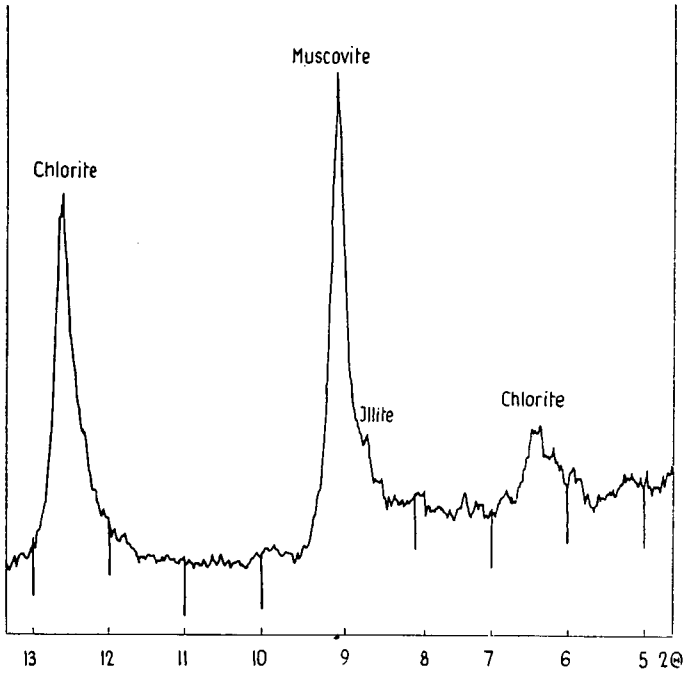

Fig. 2. Diffractogram of muscovite in presence of subordinate illite quantity in the range between 5 and 10°

In case of illite/montmorillonite$_{12}$ the peak at 12 Å will be displaced to 14 Å. When heating the sample at 550 °C, only the peak of about 10 Å of illite remains.

In case of illite/chlorite on the basis of the X-ray diffractograms it cannot be decided whether there is an intercalation or the mixture of these minerals. No change follows even in case of treatment with ethylene glycol. The same can be observed in case of chlorite/montmorillonite, too. No change appears when treating it with ethylene glycol.

Regarding the peak at around 10 Å another phenomenon should be taken into account. It appears mainly in the colloid fraction (less than 2 microns) that this peak is widely elongated and no specially intense peak develops up to the angle range of $2\vartheta \approx 10°$ (in case of CuK_α radiation, *Fig. 4)*. In these cases X-ray amorphous material of greater quantity is also present. When muscovite has been in the sample, this practically delimited the possibilities of occurrence of illite and chlorite by a peak of small angle breadth *(Fig. 5)*.

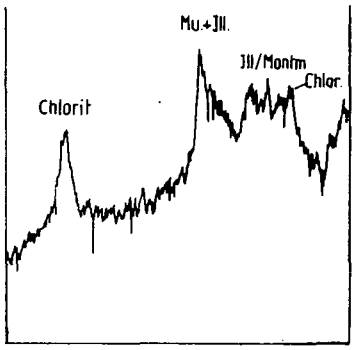

Fig. 3. Appearance of illite and illite/montmorillonite in the lower angle range of the diffractograms

In addition to the differences above several characteristic differences were observed though numerous peaks of muscovite and illite coincide. In this way, when the peak at about 4.45 Å proved to be intensive, illite was present in the sample, when not then rather muscovite could be taken into account. The relative intensity of the peak of about 5.0 Å was greater in every case when muscovite was in the sample

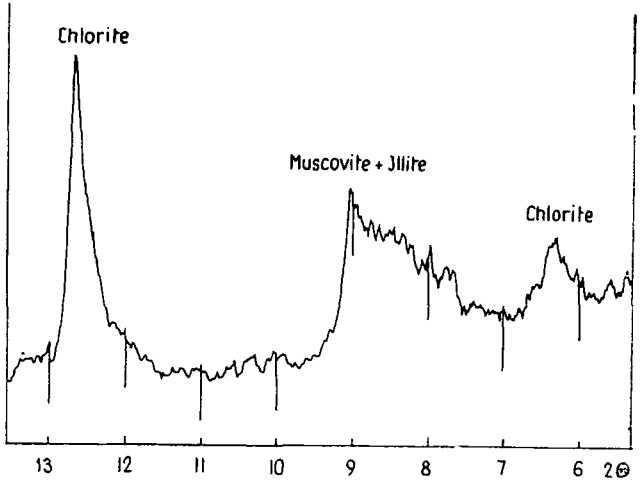

Fig. 4. X-ray diffractogram of illite and X-ray amorphous colloid fraction

TABLE I

2M (1M) index	predominantly muscovite	predominantly illite	about the same illite-muscovite	
d_{002} (d_{001})	9.821 Å	10.297 Å	9.821—10.216 Å	
I_{rel}	115	42	95	32
angle breadth	3°		3°	12°
d_{004} (d_{002})	4.952	5.008	4.952	4.952
I_{rel}	55	10	35	35
d_{110}	4.448	4.482	4.459	4.459
I_{rel}	16	50	35	35
$d_{11\bar{5}}$ (d_{112})	3.050	3.067		
	4	15		

rather than illite. The peak of about 3.08 Å was of medium relative intensity in case of illite, in that of muscovite this peak was absent.

It is interesting to compare the above-mentioned peaks' relative intensities on the basis of values measured, as well (X-ray diffractograms were recorded under the same conditions; Table 1.):

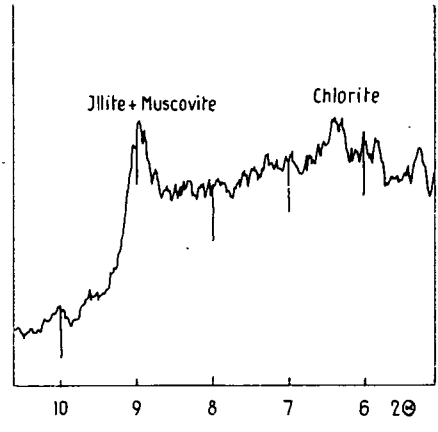

Fig. 5. Joint appearance of muscovite, illite and amorphous phase in the X-ray diffractogram

According to MAREL, H. W. [1950] in case of pure members muscovite and illite can be separated in the range of about 1.64 to 1.66 Å since muscovite gives a sharp peak while illite results in diffuse bands. In mixtures of several phases, however, e. g. in the sediments of the Great Plain no difference can be observed in this way. In this case the intensity relations of the base reflexions should be taken into account (001/002 and 004/005), if the quantity of the phases in question is large enough in the sample. Due to the changing quantity of Fe^{VI}, Mg^{VI} and Al^{VI} the regularity index of MAREL is unable for use owing to its uncertainty.

The X-ray diffractometric determination of chlorites is theoretically possible on the basis of the subsequent 002 base reflexions. The chlorites occurring in the sediments of the Great Plain do not swell, do not show adsorption and in case of

heating their lattice changes only above 500 °C. BROWN, B. E. and BAILEY, S. W. [1962] produced representative *d*-values for the frequent polytypes, but on this basis their exact determination is impossible. Regarding the intensities of the peaks $20\bar{1}$ and 201 there is significant difference. It is unfavourable, however, that in this range characteristic peaks of numerous minerals can also be found.

The isomorphous replacements influence also the distance between lattice planes. While the replacement of Si and Al decreases the distance d_{001} now the Fe^{+2} $(Mn^{+2})-Mg^{+2}$ replacement following in the octahedral layer causes changes in the *b* parameter of the cell, i. e. in case of built in of Fe^{+2} the b_0 value grows linearly. In the octahedral layer of chlorite the number of heavy atoms can be approximately determined (Fe^{+2}, Mn^{+2}, Ni^{+2}, Fe^{+3}, Cr^{+3}, Ti^{+4}) on the basis of the 00l base reflexion intensities. As to PETRUK, W. [1964] on the basis of the I 002+I 004/I 003 relation this relative number will grow parallel with the increase of the numbers of heavy atoms, when in the octahedral layers Fe^{+2} can be predominantly found. As to RISCHÁK, G. and VICZIÁN, I. [1974] the relation I 002/I 003 can be applied more favourably or in case of unfavourable line coincidence the relation I 004/I 003 is suitable. In this latter case, however, it is unfavourable that I 003 does not give an always exactly measurable peak.

Grain size also influences the base reflexions of chlorites. When this is small, the base reflexions usually widened and the d_{hkl} reflexions often disappear or occur only with very slight intensity. This is valid also of the epigenic chlorite of core samples deriving from the deep-bores of the Great Plain.

The methods elaborated for quantitative mineral determination on the basis of X-ray diffractograms are based on the measurement of base reflexion intensities, in general. Concerning the relative intensities of the single minerals there are numerous data in the literature. Since intensity is influenced by numerous factors discussed above, it is obvious that the value of the constants used in case of quantitative and semi-quantitative determinations of each minerals shows rather great deviations. The number of influencing factors grows in general from the ordered structures towards the less ordered ones. Regarding the phyllosilicates the constants mentioned in the literature were collected by RISCHÁK, G. and VICZIÁN, I. [1974]. In case of the phyllosilicates and of the inosilicates to a certain extent recently only semi-quantitative determinations are available on the basis of X-ray diffractograms owing to the great number of influencing factors.

In case of quantitative determination when giving the percentual distribution the amorphous phase should have been neglected since its quantity could not be exactly determined. When combining the diffractogrammatic method with that used by VARSÁNYI, I. [1974] the quantitative determination could be probably more exact since the amorphous phase can be easily and rapidly determined by chemical methods.

In case of quantitative determinations based on X-ray diffractograms there are such minerals the constants of which are nearly the same as to different references, thus in these cases no difficulties occurred either (quartz, calcite, dolomite, feldspar) because these are exactly identified and ordered structures. The case of phyllosilicates proved to be more troublesome. In the range of difficulties the first phenomenon was that in the investigated sediments of the Great Plain illite and muscovite occur together, moreover in numerous cases there are illite/montmorillonite mixed structures. When muscovite and illite proved to be separable, their quantitative determination was taken using the adequate constant. If this separation proved to be impossible then the constant of the predominating mineral species was taken into con-

sideration. When the intercalation of illite/montmorillonite has been of greater importance, the value of the constant was proportionally decreased.

The influence of Fe^{2+} on the peak intensities of chlorites is well-known. Thus in these cases the determination of the relative number of I 002+I 004/I 003 was done in each case. This has mostly lain within the limits given by literature, which made possible the use of uniform constants.

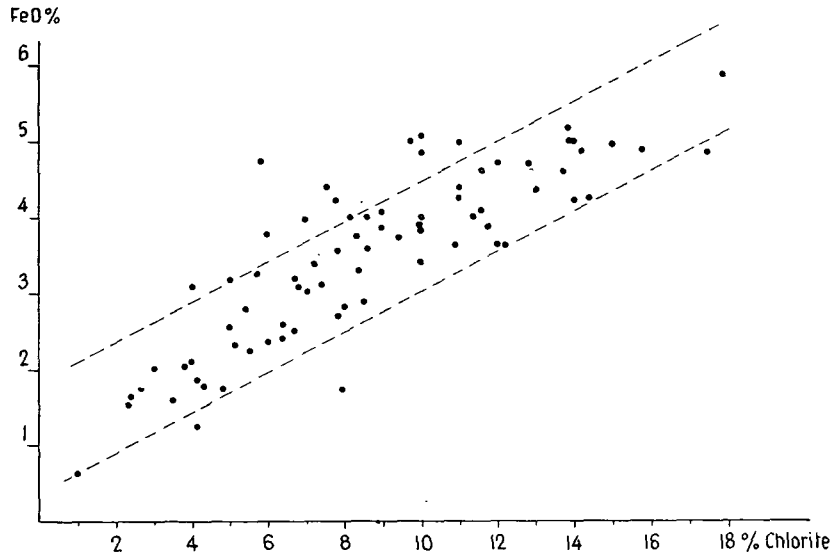

Fig. 6. Quantitative relationship between FeO and chlorite

When evaluating the diffractograms either the height of the peak or the area of peak is taken into account. In both cases the right delineation of the base line is very important, especially at the peaks of highest intensity of the phyllosilicates and feldspars. When having investigated the different grain size fractions of the samples it could be stated that in the range less than 50 microns there was no remarkable deviation between the measurements of peak intensity and area (this proved to be about 3 to 5 per cent), e. g. within the fraction less than 10 microns the two calibration curves were nearly beside each other, the curve of peak area has lain somewhat higher than that of peak height.

When investigating the average sample and the fraction less than 10 microns the quantity of chlorite has doubled in the latter fraction in every case, the quantities of illite-muscovite increased by a smaller extent. The quantities of quartz, feldspar and dolomite decreased in each case, the two latter minerals were absent in several cases.

In the investigated samples major part of Fe^{+2} is connected to chlorites. This is demonstrated by *Fig. 6.* shown the correlation between the FeO quantity determined analytically and the quantity of chlorite determined by means of X-ray diffractometry. On the basis of this it unambiguously stated that the FeO-content grows parallel with the chlorite content, in general. Where deviation occurred, the core sample had contained pyrite being determinable macroscopically as well. Deviation appeared in a negative sense in several cases, when greater quantities of fine-

grained epigenic chlorites could be taken into account, in this case the base reflexions were widened and their intensity showed considerable decrease.

Between the change of quantity of the chlorites and certain trace elements definite correlation could be determined. As regarding the illite-muscovite only a loose relationship could be determined concerning B, V, Ni and Cr, these elements show definite correlation whith chlorite. The increase of quantity of these elements given in ppm is proportional to that of the chlorites *(Fig. 7)*.

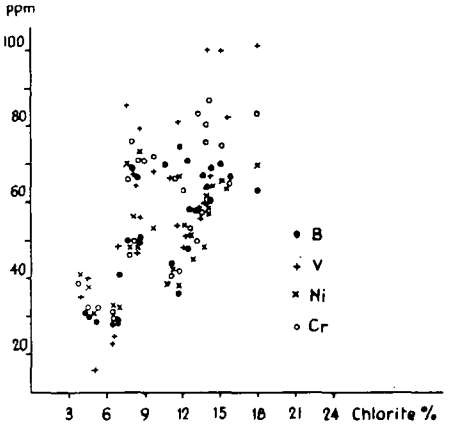

Fig. 7. Relation between the quantities of B, V, Ni and Cr with that of chlorite

A positive correlation could be determined between Sr and carbonate minerals (calcite, dolomite), too. The quantity of Sr given in ppm has proportionally increased with the increasing calcite and dolomite quantity *(Fig. 8)*.

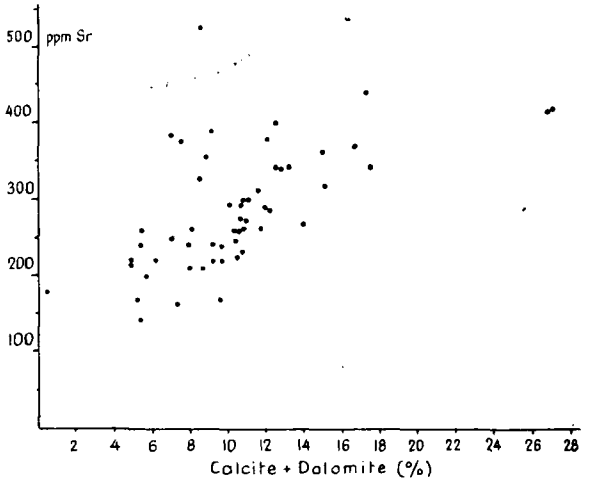

Fig. 8. Relation between the quantitative change of Sr and calcite-dolomite

In connection with the appearance of the carbonate minerals it can be stated that when investigating the sample of 10 microns the quantity of dolomite proved to be always less than in the average sample. From this phenomenon conclusion could be drawn that dolomitization followed usually during the diagenesis and the dolomite originated in this way is always coarser-grained, this it was separated out of the finer fraction.

In the samples of the „Makó depression trench" most of the feldspars being able for evaluation proved to be albite which is proved in the diffractograms by the only maximum at about 3.19 Å. The reflexion of about 3.22 Å appears locally but it is less intense and indicates the displacement of composition towards the oligoclase-andesine in the range of plagioclases. This peak, however, is always of weaker intensity. The peak at about 4.02 Å always appears in these cases.

When the quantity of feldspars remained below 5 to 6 per cent, only the albite occurred of measurable quantity, above 6 per cent the oligoclase-andesine could be usually determined, too. The increase of feldspar quantity followed mostly at the expense of muscovite-illite-quartz. The change of species and quantity of the feldspars can be attributed by all means to the change of the erosion area and this is also proved by the fact that albite and acidic plagioclase occur only in the Lower Pannonian, while in the Upper Miocene sediments only albite could be determined.

Regarding the potash-feldspars, microcline did not occur in measurable quantity (under microscope only several grains could be determined) and orthoclase could not be identified either, the characteristic peaks of high intensity were absent.

In the region of Ferencszállás the feldspar species show a more variegated assemblage. The diffractometric determinations relate both to albite, acidic plagioclase and orthoclase. Regarding their quantitative changes and distribution conditions no tendency can be demonstrated owing to the small number of data.

In both regions the quantity of feldspars considerably decreased in the fraction of 10 microns, sometimes they were absent and separated out of the original sample which related to the appearance of them in the coarser fraction.

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HYDROTHERMAL AND METASOMATIC PHENOMENA IN THE TRIASSIC LIMESTONE AREAS BORDERING ON THE ANDESITE MOUNTAIN OF THE DANUBE

GY. VITÁLIS and J. HEGYI-PAKÓ

INTRODUCTION

In the course of the limestone prospecting carried out in the western part of the Nagyszál of Vác and on the Kőszikla of Dorog, besides hydrothermal traces indicating the one-time thermal spring activity, the epigenetic dolomitization of the limestone of the Norean age was also observed. Dolomitization and other thermal water traces were associated with the hydrothermal processes following the Neogene volcanization of the andesite mountains of the Danube (Börzsöny Mountains, Mountain of Visegrád). The magnesium ions of the several hundred metres thick Carnian dolomite deposited under the limestone group of the Norean age were elutriated by the hydrotherms, then getting them ascendingly into the crevices of the limestone, they caused the dolomitization of the limestone to different extent. Practically, the traces of the thermal spring activity taking place from the Middle-Miocene epoch to the end of the Pleistocene epoch can be investigated both in the limestone and volcanic group, as well as in the covering formation in the entire region.

After the Nagyszál of Vác, the traces of hydrothermal effects observed also on the Kőszikla of Dorog, called our attention to investigate the developments of the limestone areas bordering on the andesite mountains of the Danube as well. By doing so, it was possible to record the rock alterations of hydrothermal origin associated with volcanic activity on the one hand and to get a basis for studying the metasomatic sulfide mineralization probably taking place on the border of the Triassic limestone and the Neogene andesite on the other.

THE GEOLOGICAL SETTING AND EVOLUTION OF THE AREA

The geological setting of the andesite mountains of the Danube and the adjacent limestone areas is summarized by the reconnaissance geological map *(Fig. 1)* and geological section *(Fig. 2)*. The evolution of the area is outlined in the following.

During the *Upper Triassic epoch* in the entire area continuous marine deposits, on the Carnian stage dolomite, in the Norean stage, in the region of Dorog, limestone white dolomite shelves, then limestone of Dachstein; in the region of Vác limestone of the Dachstein type are formed. At the end of the Triassic period, the entire area rises to a minor extent under the effect of Old-Cimmerian movements.

In the region of Dorog, sedimentation (limestone — marl) continues *in the Jurassic period*, the region of Vác is already a continent since the end of the Triassic

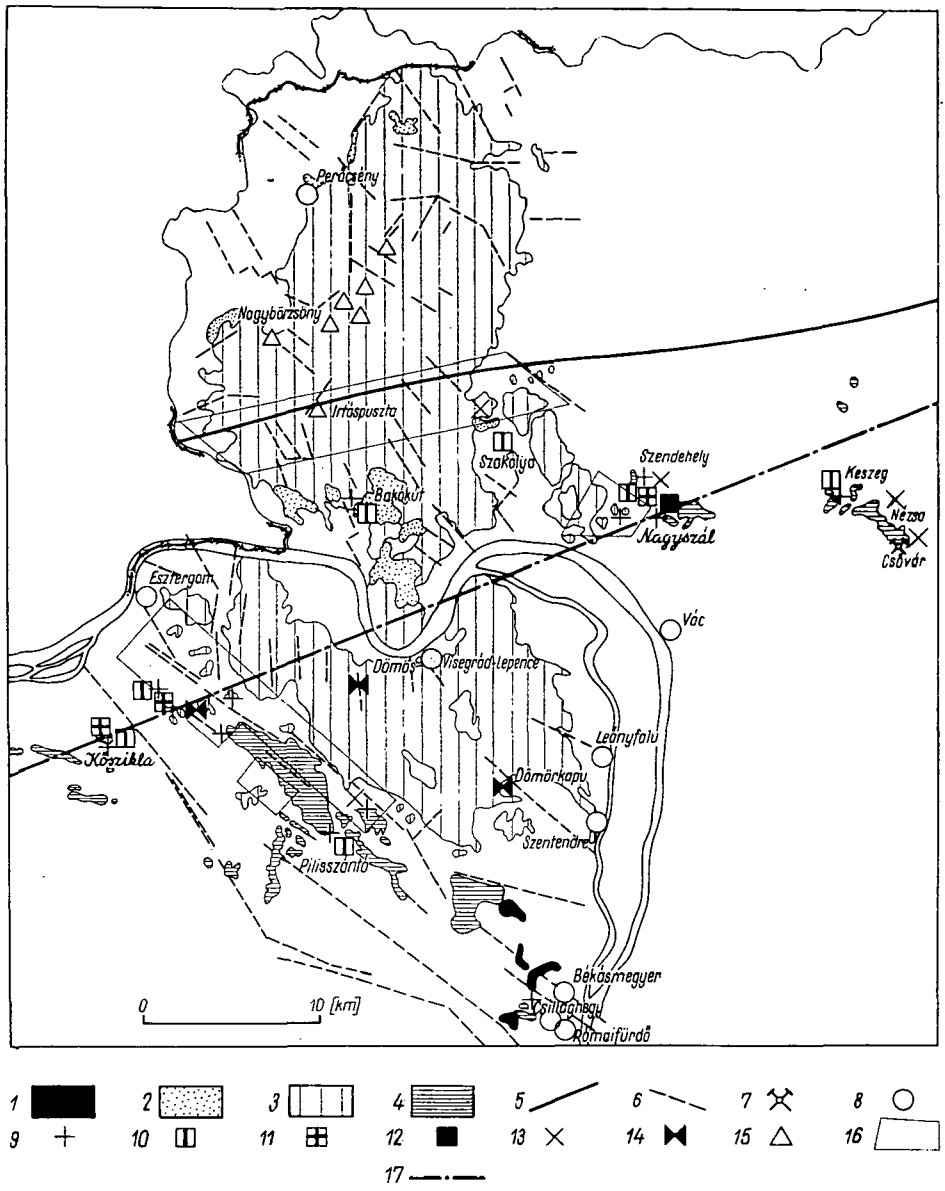

Fig. 1. Reconnaissance geological map of the andesite mountains of the Danube and the adjacent limestone areas (After the 1:200 000 map detail of the hydrogeological map of Hungary, with supplementation) *1.* Fresh-water limestone *(Pleistocene)*, *2.* Lajta limestone *(Neogene)*, *3.* Andesite — andesite tuff *(Neogene)*, *4.* Limestone *(Triassic)* on the surface; *5.* Border of Paleozoic and Mesozoic basement below the surface; *6.* Aquiferous break; *7.* MÁFI perspective prospecting bore; *8.* Thermal well and lukewarm spring; *9.* Trace of thermal spring; *10—12.* Formed by hydrothermal metasomatism: 10. Dolomitic limestone, *11.* Calciferous dolomite, *12.* Dolomite; *13.* Limonite of thermal spring origin; *14.* Pyrite impregnation; *15.* Sulfide mineralization; *16.* Prospective area from the point of view of metasomatic sulfide mineralization; *17.* Section line.

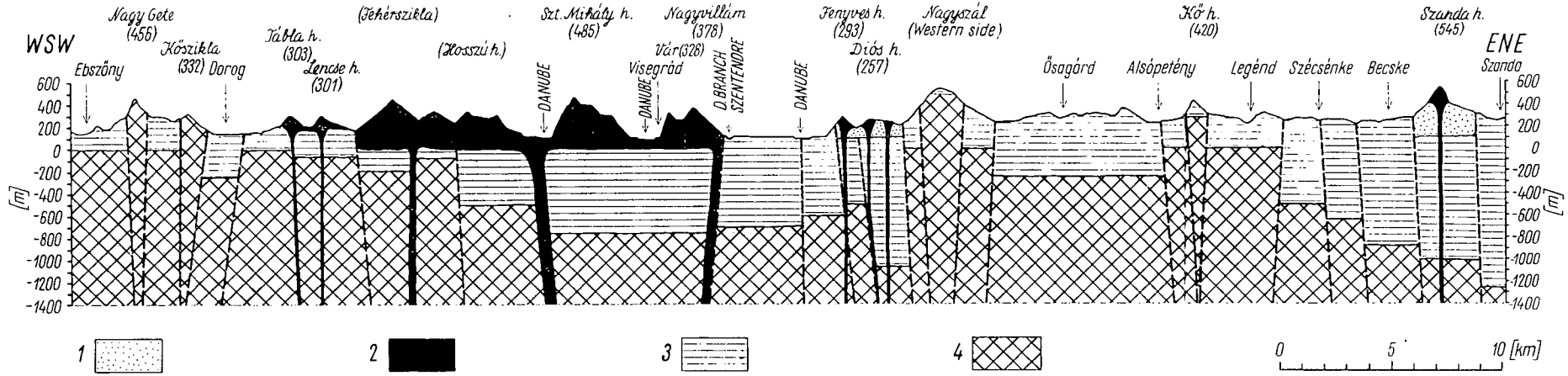

Fig. 2. Draft geological section of the andesite mountains of the Danube and their surrounding (After the 1:300 000 geological map of Hungary and the uncovered, scale 1:500 000 geological map of the Paleozoic and Mesozoic formations of Hungary, with contraction) *1.* Clay, sand, sandstone, clayey marl, limestone *(Neogene)*; *2.* Andesite and andesite tuff *(Neogene)*; *3.* Sand, sandstone, clay, clayey marl, marl, limestone *(Palaeogene)*; *4.* Limestone, dolomite *(Triassic)*.

Summary table of chemical and mineralogical-petrographical analyses

TABLE 1

Name and place of origin of the rock	Chemical composition									Mineral composition on the basis of			Trace elements		
	Ign. loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	Thermal	Radiographic	Thin section	100—1000	50—100	<50
	weight percent									examination			g/t		
Hydrothermally decomposed limestone, Dorog, Strázsa Mountain Quarry	43,86	0,27	0,10	0,17	55,77	0,10	<0,10	<0,10	0,03	calcite	calcite	calcite, dolomite		Sr	
Saccharoidal algaic limestone, Keszeg Limestone Quarry	43,87	0,10	0,10	0,04	55,58	0,10	<0,10	<0,10	0,34	calcite	calcite	calcite			Sr
Hydrothermally decomposed striated limestone, Keszeg Limestone Quarry	43,87	0,20	0,10	0,03	55,49	0,10	<0,10	<0,10	0,32	calcite	calcite	calcite			Sr, Ba
Pyritic limestone, Dorog Strázsa Mountain Quarry	43,28	1,12	0,10	0,11	55,27	0,10	<0,10	<0,10	0,03	calcite, pyrite	calcite, quartz, kaolinite	calcite		Sr, As	
Hydrothermally decomposed limestone, Dorog, entrance of Sátorkőpuszta Cave	44,01	0,12	0,09	0,10	54,72	0,90	<0,10	<0,10	0,04	calcite	calcite, quartz	calcite		Sr	
Hydrothermally decomposed limestone, Keszeg Limestone Quarry	43,09	1,40	0,46	0,19	54,68	0,10	<0,10	<0,10	0,39	calcite	calcite	calcite, quartz			Sr
Hydrothermal vein filling between Keszeg and Csővár	40,14	5,65	1,23	2,66	49,56	0,10	<0,10	<0,10	0,37	calcite, dolomite	calcite				Sr, Rb, Ba
Striated, dolomitic limestone, Pilisszántó, Pilis Mountain Limestone Quarry	44,47	0,33	0,10	0,07	51,90	3,00	<0,10	<0,10	0,11	calcite, dolomite	calcite, dolomite	calcite		Sr	
Dolomitic limestone, Dorog, Small Strázsa Mountain	44,30	0,06	0,10	0,11	52,64	3,10	<0,10	<0,10	0,02	calcite, dolomite	calcite, dolomite	calcite		Sr	
Dolomitic limestone, Keszeg, drilling No. 6, 14,2 m	45,40	0,10	0,31	0,17	45,61	8,41	<0,10	<0,10	0,01	calcite, dolomite	calcite, dolomite, quartz	calcite, dolomite		Sr	
Saccharoidal, dolomitic limestone, Dorog, Strázsa Mountain Quarry	49,43	0,22	0,10	0,46	44,57	9,49	<0,10	<0,10	0,02	calcite, dolomite	calcite, dolomite	calcite, dolomite		Sr	
Calciferous dolomite, Dorog, Small Strázsa Mountain	46,02	0,33	0,10	0,11	40,32	13,20	<0,10	<0,10	0,02	calcite, dolomite	dolomite, calcite	dolomite, calcite		Sr	
Hydrothermally decomposed andesite, Piliszentlélek, Esztergom—Dobogókő highway 23,8 km	2,54	72,12	15,91	1,12	2,65	0,20	2,30	2,57	0,31	clay mineral	feldspar, quartz, montmorillonite, illite, kaolinite	plagioclase, garnet, biotite	Sr	Rb	Ba
Striated, hydrothermally decomposed, garnetoid biotite andesite, Pilisszentlélek, Esztergom—Dobogókő highway 23,8	3,28	71,20	15,10	2,44	2,65	0,10	2,09	2,36	0,54	clay mineral	feldspar, quartz, montmorillonite, illite	plagioclase, garnet, biotite	Sr	Rb	Ba
Biotite-amphibole andesite, Vác, Diós Mountain excavation between 42—43 km	1,22	61,29	17,85	5,61	7,42	1,68	2,46	1,68	0,50	clay mineral	feldspar, amphibole	plagioclase, biotite, amphibole	Sr	Ba	Rb
Hydrothermally decomposed andesite tuff, Vác, Diós Mountain excavation between 42—43 km	1,80	59,99	18,03	6,13	7,70	2,10	2,39	1,54	0,30	clay mineral	feldspar, amphibole, montmorillonite	plagioclase, augite, biotite		Sr	Ba, Rb, Mn

period. At the end of the Jurassic period, in consequence of the New-Cimmerian movements, a dry period, then erosion takes place in the entire area.

In the Lower Cretaceous period, the region of Dorog is covered by sea again, then the entire area is a continent. At the border of the Lower and Upper Cretaceous periods in the Austrian, then during the Subhercyn orogenesis, karst formation, and at the end of the Cretaceous period bauxite formation (Nézsa), then erosion take place.

During the movements of the Laramide, *in the Lower Eocene period* subsidence, in the region of Dorog and Vác (Kosd), and partly between the two areas as well, brown coal formation, then marine transgression (clayey marl — marl — limestone), repeated in the *Middle and Upper Eocene periods* too, follow. Due to the Pyrenean movements (Upper Eocene), the series of Eocene layers which got into a deeper position are more complete because it was more protected against the infra-Oligocene denudation.

During the *Lower Oligocene* period, in the region of Dorog large-scale erosion (infra-Oligocene denudation) takes place, in the region of Vác sandstone of „Hárshegy" and conglomerate; in the *Middle Oligocene period*, of the entire area, Foraminiferous clay — clayey marl ("clay of Kiscell"), in the *Upper Oligocene period* sand, sandstone and clay are formed.

In the region of Dorog (due to the orogeny of Sava) Miocene deposits are not known, in other parts of the area, the formations of *Burdigalian* and *Helvetian* are of mechanical character. The andesite volcanism of the Danube region starts as early as the middle of the Helvetian stage, however, the main mass of the mountain emerges to the surface in the *Lower Tortonian substage*. The volcanism is accompanied in some places by sulfide mineralization containing precious metals (Nagybörzsöny). The covering formation of the volcanic group is Lajta limestone of the *Upper Tortonian substage*, and the *Sarmatian stage* is represented by clayey marl and limestone.

The post-volcanic hydrothermal effects caused sulfide mineral impregnations, mineral veins in the andesite group and dolomitization in the adjacent Triassic limestone area. It is probable that scarnic and polymetallic sulfide mineralization took place at the border of limestone and andesite.

Owing to the hydrothermal effects, siliceous sinter and fresh-water limestone (Szokolya) are formed, and in the Lajta limestone, deposited on the andesite group, only slight dolomitization (Zebegény) can be observed. The siliceous binding material of the limestone of "Hárshegy" can also be associated with the post-volcanic activity.

The *Lower Pannonian* clayey and the *Upper Pannonian* sandy — clayey formations are deposited only at the edge of the Danube andesite mountains rising as an island from the Pannonian internal lake and at the edge of the surrounding Mesozoic limestone — dolomite islands. Thermal water activity continues in the Pliocene period, too. The break through of the Danube at Visegrád starts at the end of the Pliocene period.

During the *Pleistocene* thermal water activity, dolomite pulverization and rock decomposition is caused by the hot, then by the moderately warm karstic springs welling up along the aquiferous cracks; calcite veins, fresh-water limestone and labyrinths with spherical cavities are formed. During the young post-Pannonian movements, the entire area rises to its present height, thermal water activity ceases on the elevated parts, erosion and karst formation continue.

The present *(Holocene)* state is shown by the geological section illustrated in *Fig. 2.*

THE PLACE OF ORIGIN OF THE SAMPLES INVESTIGATED

The rock samples documenting the hydrothermal and metasomatic effects were collected in the area of the Triassic island blocks, in the area of the Szendehely blocks, as well as in the area of the block group of Keszeg — Csővár. The samples originating from the Triassic limestone group of the Pilus Mountain were taken from the quarries on the Mt. Kis Strázsa and Mt. Nagy Strázsa and in the region of Kesztölc, Pilisszentkereszt and Pilisszántó along the Kétágúhegy — Pilis — Hosszúhegy range.

For the investigation of the hydrothermally decomposed Neogene andesite near the Mesozoic limestone group, fresh and more decomposed andesite varieties were also collected from the road cuts of the Esztergom — Dobogókő highway, in the region Pilisszentlélek and from the Mt. Tábla between the Strázsa Mount and Kétágúhegy Mountain in the region of Dorog.

RESULTS OF MATERIAL TESTING

The samples were subjected to complete chemical analysis, thermal, radiographic, semi-quantitative X-ray spectrometric and microscopic testing. The more important mineralogical — petrographical characteristics determined on the basis of the complete chemical analyses and instrumental tests — according to genetic types — are summarized by Table 1.

The chemical and instrumental analyses were made at the Department of Silicate Chemistry of the Central Research and Planning Institute for the Silicate Industry. The photographs of the rock thin-sections with crossed nicols were taken and were evaluated by I. CSORDÁS, at the Mineralogical and Petrographical Department of the Technical University of Heavy Industries, and the semi-quantitative X-ray spectrographic analyses were carried out by DR. L. BOGNÁR, at the Mineralogical Department of the Eötvös Loránd University.

Of the thin-section, photographs bringing best into relief the genetic characteristics of the hydrothermal rock alterations, are shown. The pictures shown represent partly the individual phases of the hydrothermal phenomena, partly — by covering several areas — the process of the phenomena taking place on both sides of the andesite mountain of the Danube. The explanation of the rock thin-sections is given below.

PLATE I

Photomicrograph 1. Fine-grained limestone broken under more intensive dynamic effect. The network of veins consists of coarse crystalline calcite.

Photomicrograph 2. Pellets hidden in pelitic micrite basic material. The entire material is crossed by a network of calcite and siliceous diffuse veins.

PLATE I. *1.* Thin-section of hydrothermally decomposed limestone (Dorog, Mount Strázsa); *2.* Thin-section of hydrothermally decomposed limestone (Dorog, entrance of the cave of Sátorkő-puszta) *3.* Striated, dolomitic limestone (Pilisszántó, limestone quarry of Pilis Mountain) *4.* Thin-section of dolomitic limestone (Dorog, Mount Kis Strázsa)


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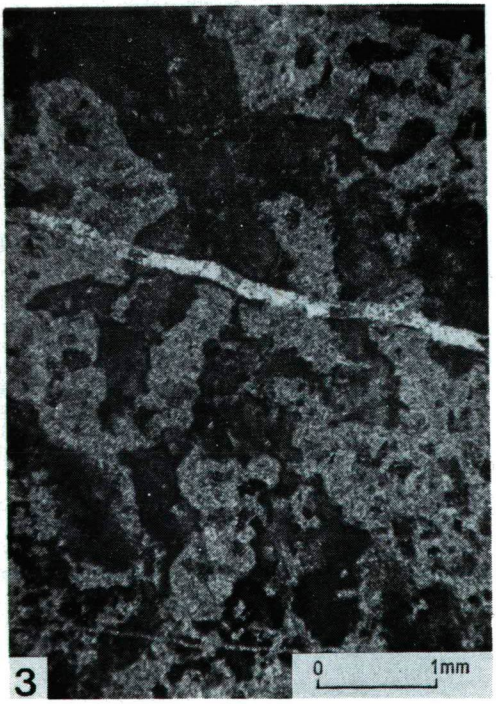
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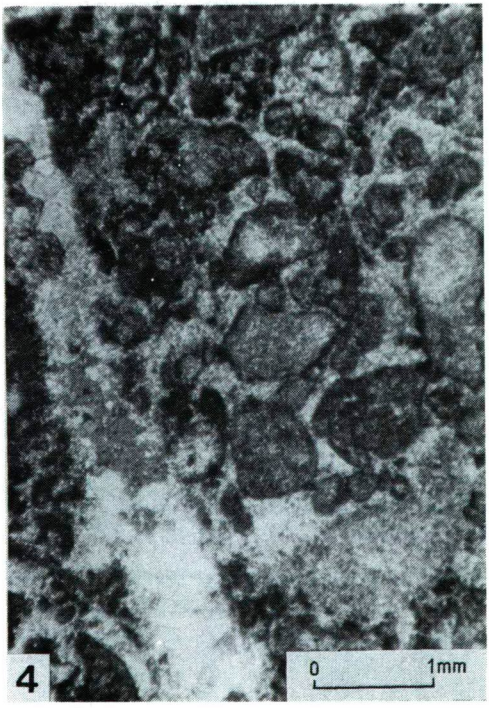
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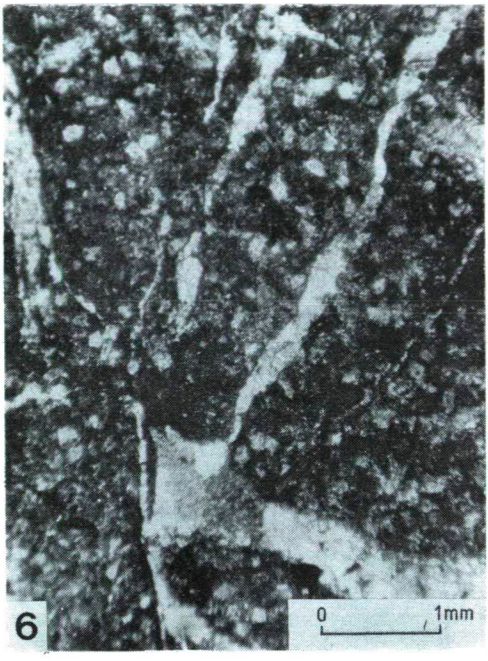
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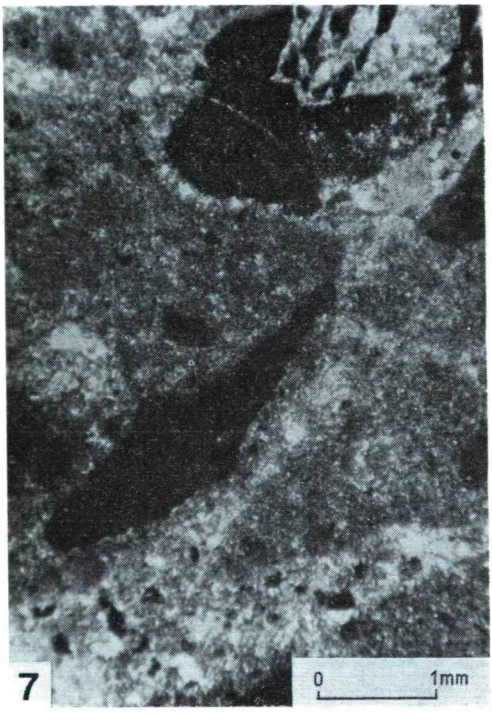
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Photomicrograph 3. Pelitic, microcrystalline limestone with lithographic structure transformed under hydrothermal effect, with reabsorptive and recrystallized structural marks.

Photomicrograph 4. Pelletic biomicrite with epigenetic calcite filling, with a finer network of veins in some places.

PLATE II

Photomicrograph 5. Oopelletic, algaic biomicrite with a string network of spathic veins, with cavernous, nesty pore cement.

Photomicrograph 6. The basic material was transformed into coarser-grained dolosparite along the diffuse vein network.

Photomicrographs 7 and 8. In basic material consisting of pelitic dolomicrite, darker intraclastic inclusions, interwoven with coarse crystalline calcite veins. In some places, the microbreccias of the intraclastic details and their resorption, respectively, can be observed.

The microphotographs demonstrate the alterations caused by the hydrotherms, the epigenetic calcite and siliceous filling and dolomitization well.

Metasomatic dolomitization manifests itself first along fissures, then penetrating into the inner parts of the rock, in widening, nesty, bossy impregnations. Its dimension varies in a wide range (from microscopic to metric order of magnitude). The most varied structural character is displayed by the intermediate rock types (e. g. dolomitic limestone varieties).

It should be also noted in connection with the material tests that the higher CaO content of the andesite samples from the Diós Mountain of Vác are indicative of the carbonation of the andesite group. The K_2O quantity of the hydrothermally decomposed andesite originating from the region of Pilisszentlélek (2,36 and 2,57%) falls between the normal (intact) andesite and the hydrothermally intensively decomposed andesite (Table 1). These provide data for studying the petrometallogenetic evolution of the area, too. The epigenetic dolomitization of the Triassic limestone, as well as the carbonation of the Neogene andesite and its presumed potassium metasomatism are pre- and synmetallogenetic.

PRACTICAL CONCLUSIONS

The following practical conclusions are drawn from the comparison of geological observations and the results of material testing.

Metasomatic dolomitization is indicative of hydrotherms originating from a greater depth, whereas simple hydrothermal decomposition is possible from thermal water originating from a smaller depth, too.

Metasomatic dolomitization is completed by the end of the Pliocene period, the thermal springs causing simple hydrothermal rock alterations are most intensive in the Pleistocene period. The former is connected with volcanic post-activity, the

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PLATE II. *5.* Thin-section of dolomitic limestone (Keszeg, bore No. 6, 14,2 m) *6.* Thin-section of dolomitic limestone with saccharoidal structure (Dorog, Mount Strázsa) *7.* Thin-section of calciferous dolomite (Dorog, Mount Kis Strázsa) *8.* Thin-section of calciferous dolomite (Dorog, Mount Kis Strázsa)

latter ones indicate the activity of first hot, then lukewarm karst springs and thermal springs mixed with cavern water, respectively.

In the Mesozoic basement areas *(Fig. 1)*, the areas suitable for the development of thermal water can be allocated by means of the traces of one-time thermal springs. Of these, thermal water can be developed at a smaller depth below the surface in the region of Dorog and at a greater depth below the surface in the other areas.

On the basis of the appearance of calciferous dolomite, active zones can be allocated from the point of view of metasomatic dolomitization. It can be concluded from the fact of dolomitization that metasomatic sulfide mineralization is possible on the border of the Mesozoic limestone and Neogene andesite groups, e. g. similar to the one of Óradna. The borders of the prospective areas (on the basis of taking the active zones known so far from the point of view of metasomatic dolomitization and the large structure into consideration) are indicated on a reconnaissance geological map *(Fig. 1)*.

Attention is called to hydrothermal mineralization probably located at a greater depth below the surface by the limonite segregations of the carbonate rocks (Szendehely, Csővár, Pilisszentkereszt, etc.), by the pyrite scatterings of the andesite (Dömös, Mt. Tábla), as well as by the sulfide mineralizations (Nagybörzsöny, Irtáspuszta), moreover by the trace elements of the thermal spring deposits and hydrothermally decomposed rock varieties.

In the industrial utilization of limestone, the fact of metasomatic dolomitization — with special regard to the irregular seam conditions — deserves attention in any case.

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SOME SORPTION PROPERTIES OF CLINOPTILOLITIZATED PYROCLASTICS OF TOKAJ MOUNTAINS, HUNGARY

É. DONÁTH, L. GRÁBER and O. LIBOR

INTRODUCTION

Clinoptilolite is one of the most wide-spread zeolites originating from pyroclastics. Numerous occurrences of the Soviet Union, Japan, New-Zealand etc. are introduced in the literature, geological, genetic, geochemical, etc. characterization is available regarding these beds. These occurrences have special importance since then specific features of clinoptilolite are known which result in its industrial significance and make possible its ever growing utilization [MERCER *et al.*, 1970].

The clinoptilolite occurrence of the Tokaj Mountains, Hungary is interesting not only from the point of view of geology, metallogeny and mineralogy-petrology and is worthy of research also in the future, but the recognition of its exploitability and manifold applicability proved to be also important. The ever growing utilization both in Hungary and in abroad favours the further research of the area, of the rock and of the clinoptilolite itself.

On the afore-mentioned bases investigations were performed partly to determine the mineralogical, structural features of the clinoptylolitizated pyroclastics, partly to discover the sorption features of the original rock and preparates made from it. These investigations have both theoretical and practical significance.

It is well-known that clinoptilolite is used for different industrial purposes (catalysator, adsorbent, ion-exchanger, molecule-sieve). Consequently, the knowledge of the mineral composition, of the ratio of composition, of the features of structural changes following due to heat treatment, further the recognition of the adsorption features being connected to these peculiarities gives the possibility to discover the structural (theoretical) features and promotes the wider utilization.

NEMECZ and VARJÚ [1962] demonstrated in the elaboration of the mineralogy-petrology that investigating several occurrences of zeolitized volcanic tuff known as "clinoptilolite", this is a rock consisting of several minerals: clinoptylolite, adularia, cristobalite, quartz and occasionally montmorillonite.

In the course of our investigations the Hungarian "clinoptilolite" was investigated by X-ray diffractometer, derivatograph and infrared spectroscope, its total chemical analysis was performed and its trace element content was determined by Q-24 spectrograph (12).

The material of two not totally similar clinoptilolite occurrence of the Tokaj Mountains was investigated by X-ray diffractometer, and in all cases not only the unheated but the heated samples (up to 200, 300, 500, 600, 800 and 1000 °C, sample No. 1) as well as the sample heated up to 600 °C (on which the ion exchange and adsorption investigations were done, sample No. 2) were controlled.

As regarding the mineral composition of the two unheated clinoptilolites, they showed smaller differences. In the sample No. 1 in addition to the amorphous phase adularia, quartz, cristobalite and less montmorillonite were identified, in the other sample (No. 2) no amorphous phase was found, and in addition to clinoptilolite adularia, quartz and cristobalite were identified.

EXPERIMENTAL PART

The composition of clinoptilolite

On the basis of the X-ray diffractometric records of the heated material of sample No. 1 it was obvious that in every material of clinoptilolite heated under 600 °C it could be identified by the original intensity, while in the material heated up to 600 °C it showed smaller decrease of intensity.

Though 1—2 d(Å) values could be identified in the material heated up to 1000 °C, this sample became essentially X-ray amorphous.

When heating at 300 °C the mineral asemblage quartz, cristobalite, adularia, clinoptilolite of the sample No. 1, in the unheated material these minerals could be identified by smaller decrease in intensity, except quartz *(Fig. 1)*.

In addition to the chemical analysis, quantitative determination was done from the unheated X-ray diffractometric record of the sample No. 1 with the aid of the chemical analysis.

Data of the chemical analysis:

SiO_2	69.12
Al_2O_3	11.60
TiO_2	0.39
Fe_2O_3	1.39
MnO	0.01
MgO	0.18
CaO	1.27
Na_2O	0.17
K_2O	5.50
	98.51 per cent

From this composition theoretically
35 per cent clinoptilolite
34 per cent adularia
30 per cent cristobalite, quartz and amorphous material could be calculated.

TABLE 1

Mineral	Unheated	Heated to				
		200	300	400	500	600 °C
		percentual distribution				
clinoptilolite	35	34.6	32.2	28.1	30.3	29,8
adularia	34	20.8	25.4	17.4	19.2	19.2
amorphous and SiO_2 varieties	30	50	39	12.5	1.3	32.8

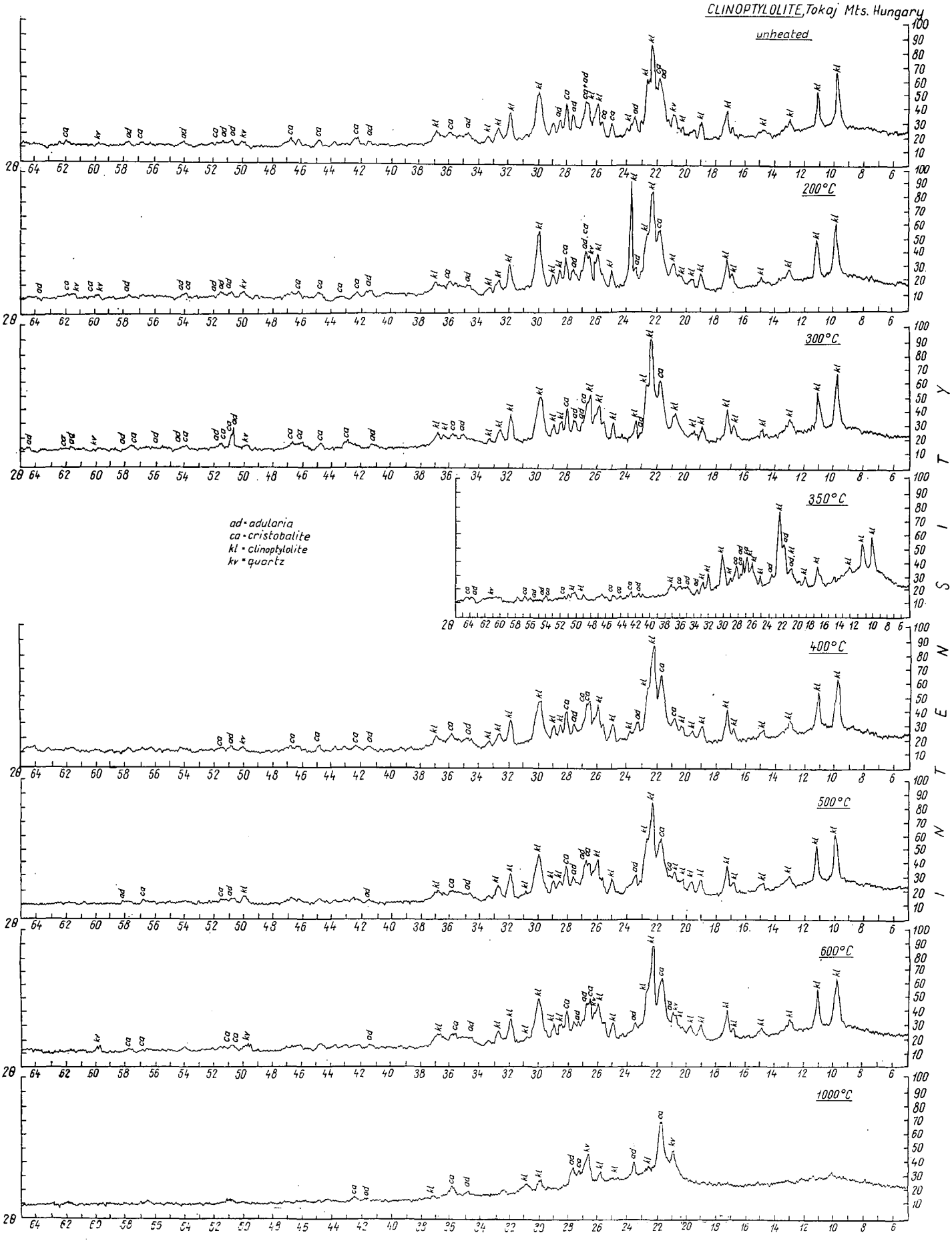

Fig. 1. Diffractometric records of unheated and heated clinoptilolite, Tokaj Mts., Hungary

TABLE 2

Siderophile elements			Chalcophile elements						
Fe	Co	Ni	Ag	Cu	Zn	Ge	Sn	Pb	As
+	0	tr	0	tr	tr	0	tr	tr	0

Litophile						Pegmatophile elements									Sedimentophile	
Li	Na	K	Cs	Ca	Mg	Sr	Ba	Ti	V	Ga	Cr	Mo	Mn	Be	B	
0	+	+ +	0	+	tr	tr	tr	tr	tr	tr	tr	0	tr	tr	tr	

note: tr = traces

On this basis using the measured areas calculated composition was determined graphically.

The graphically recalculated composition shown in the data of Table 1. indicates the quantitative changes of the single minerals compared with one another.

The trace element content is given in the Table 2.

Investigation of the water content of clinoptilolite

The thermal decomposition of clinoptilolite was followed by derivatograph. On the basis of *Fig. 2* its water-release is continuous up to 500 °C, with slight endothermal deepening at 120 and 656 °C.

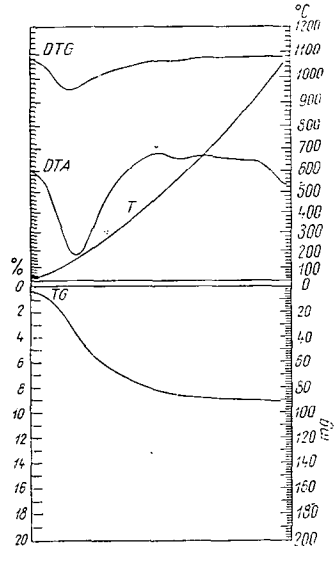

Fig. 2. Derivatogram of "clinoptilolite", Tokaj Mts., Hungary

On the basis of infrared spectroscopic investigations the adsorption bands of the unheated material as well as of the material heated up ot 350 and 700 °C of the clinoptilolite are nearly the same. In addition to the adsorption bands characteristic of the water content of OH—Al, the cation-OH band around 670 cm^{-1} also appeared. In the adsorption band range between 3600 and 3400 cm^{-1} two adsorptions (at 3530 and 3240 cm^{-1}) relate to the fact that the water of clinoptilolite is bound in several forms. As regarding the character of its water content it was stated that the arrangement of the water molecules is partly around the Al-ion, partly around the cations as a hydrate sphere. On the basis of the absorption bands between 400 to 1000 cm^{-1} being characteristic of the silicate bond its structure is similar to that of the inosilicates. The absorption range of 670 cm^{-1} being characteristic of the cations indicates considerable sodium and potassium built-in into the lattice. The intense band of 8000 cm^{-1} characteristic of the feldspars is due to the adularia content of the clinoptilolite *(Fig. 3)*.

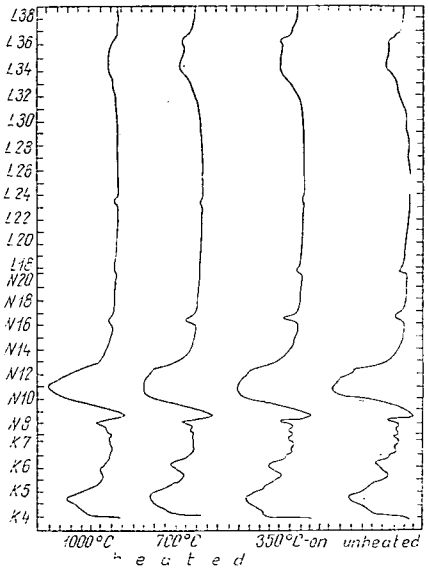

Fig. 3. Infrared spectra of "clinoptilolite", Tokaj Mts., Hungary

The infrared spectrum showed both structure modification and change in water content of the clinoptilolite only in cases heated up to 1000 °C.

Investigation of the sorption capacity of clinoptilolite

These investigations were performed on the clinoptilolite-bearing rock of the Tokaj Mountains, Hungary (in the following clinoptilolite) and on the so-called "clinosorb" material produced from it by the Reanal Fine Chemicals Factory, Budapest.

These materials were previously treated by ammonium-chloride solution for several hours, then they were heated at 400 °C. The products obtained in this way were brought into contact with different electrolyte solutions. During the investigations the equipment demonstrated in *Fig. 4* was used.

TABLE 3

Investigation of the ion exchange of clinoptilolite in diluted solution of ammonium chloride

Adsorbent	Concentration NH_4Cl mmol/l		Specific conductivity of the solution, μS		Specific conductivity of the solution calculated from ion mobility, μS		Duration of measurement	Cell potential between silver-glass electrode, mV		Apparent pH		Adsorbent NH^{+4} capacity mmol/100 g
	initial	final	initial	final	initial	final		initial	final	initial	final	
1	2	3	4	5	6	7	8	9	10	11	12	13
clinosorb, original	1.35		197	204	184		7.5	−7	+62	5.94	7.52	
clinosorb, original	1.353		205	227	184		7.15	−55	+57	6.75	7.05	
flushed, heated clinoptilolite	1.454		198	201	200		7.0	−38	+60	5.38	7.13	
activated clinosorb	ion-free boiled water		3,1	7,0	184		6.0	+33	+9	6.70	6.18	
clinosorb, activated	1.35	0.25	192	361		466	6.0	−3	−147	6.02	3.58	8.10
activated clinoptilolite	1.39	0.29	197	392	189	472	5.5	−37	−151	5.40	3.50	8.00

RESULTS OF THE MEASUREMENTS AND CONCLUSIONS

The first measurements should have provide data on the fact that the ion exchange feature of the natural resp. activated clinoptilolite is the same or not. Thus the phenomenon was investigated that how the natural and activated clinoptilolites taken into a given ammonium-chloride solution of given concentration change the electrochemical features of the solutions being in interaction with them, resp. how they change the concentration of the NH_4Cl solution. *Figs. 5* and *6* contain the results of these measurements. In the solution interacting with the inactivated clinoptilolite the electrode potential increases at the beginning (during about 2 to 3 hours), then it becomes constant. In case of the activated zeolites, however, the electrode potential considerably decreases at the beginning (during about 30 to 40 minutes) and becomes constant only leaving this time *(Fig. 5)*.

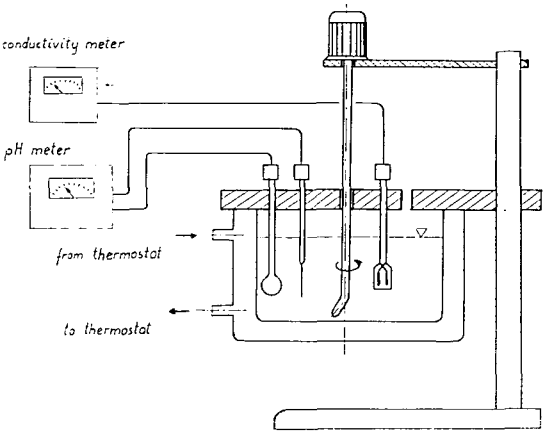

Fig. 4. Equipment for electrochemical investigation

The starting resp. equilibrium values of the electrode potential are involved in the columns 9—12 of Table 3, in case of sorbents of different features. It is obvious from the figure that the conductivity of the ammonium-chloride solution did not change in case of natural zeolites, in presence of activated sorbents, however, it considerably increased during about two hours, then it became constant *(Fig. 6)*. The columns 4 and 5 of Table 3 contains the starting and equilibrium specific conductivities of the solutions interacting with the sorbents.

On the basis of the obtained results conclusion may be drawn that at the active places of the natural sorbents such ions were originally present the electrochemical features of which are nearly the same than those of the ammonium ion. The sorbents, however, activated by us contained such contra-ions which had opposite elektrochemical features. The considerable increase in specific conductivity and strong decrease in electrode potential (and pH) show that after activation in the active places of the sorbents there should be hydrogen ions. The sorbents treated previously with ammonium ions lost ammonium at 400 °C, and transformed into hydrogen-zeolites.

The specific conductivity of different rate of the activated sorbents shown in the *Fig. 6* (curve a, b) is due to the different grain size.

The other aim of the investigations was to obtain data that how the ammonium is bound on the clinoptilolite. It was plausible that depending on the different

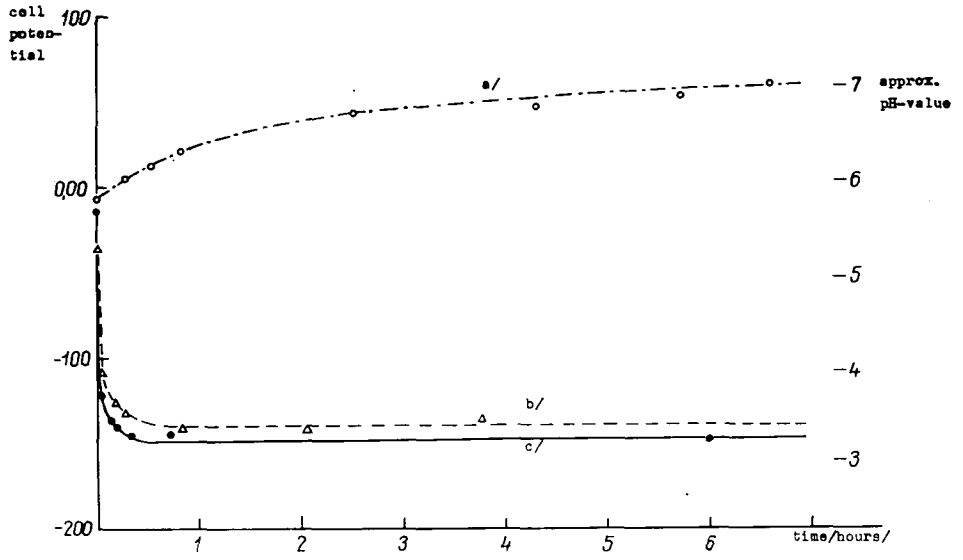

Fig. 5. Following of adsorption, resp. ion exchange on clinoptilolite by electrode potential measurement. *a)* 1 g clinosorb in 80 ml ammonium chloride solution of 1,35 mmol/litre; *b)* 1 g activated clinoptilolite in 73 ml ammonium chloride solution of 1.39 mmol/litre; *c)* 1 g activated clinosorb in 73 ml ammonium chloride solution of 1.35 mmol/litre

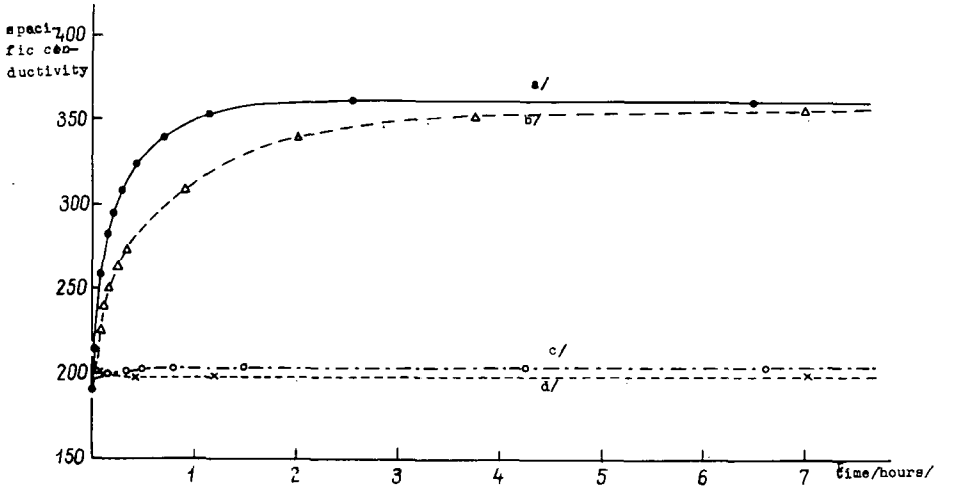

Fig. 6. Following of adsorption, resp. ion exchange on clinoptilolite by conductivity measurement. *a)* 1 g activated clinosorb in 73 ml ammonium chloride solution of 1.35 mmol/litre; *b)* 1 g activated clinoptilolite in 73 ml ammonium chloride solution of 1.39 mmol/litre; *c)* 1 g clinosorb in 80 ml ammonium chloride solution of 1.35 mmol/litre; *d)* 1 g clinoptilolite in 80 ml ammonium chloride solution of 1.39 mmol/litre

conditions in addition to ion exchange adsorption may also follow. Thus, in favour of the observation of the change of concentration of the starting ammonium solution, in case of every electrochemical measurement the concentration of ammonium ion of the solutions of equilibrium state was also determined (7). These data are shown in the columns 2 and 3 of Table 3.

On the basis of these data calculations were performed to determine that the conductivity of the solutions in questions obtained by calculation shows any deviations from the measured values or not. The following relation served as a basis of calculations (WEAST, 1967—68).:

$$\varkappa = \sum_i \frac{c_i u_i}{1000},$$

where $\varkappa$ = specific conductivity, Sm^{-1}.
c_i = ion-concentration. gequ/l.
u_i = relative ion mobility.

The column 6, 7 of Table 3 contains the results obtained in this way.

Data show that the measured and calculated specific conductivities of the starting ammonium chloride solutions are nearly the same. The specific conductivity values, resp. both the measured and the calculated ones of the equilibrium solutions being in interaction with the activated zeolites show considerable differences (5,7 column, Table 3). Supposing that all the ammonium ions being absent in the solutions were replaced hydrogen ions as contra-ions, the value of calculated specific conductivity proved to be the values given in the column 7 of Table 3. These values are higher than the measured ones in case of both sorbents. It may be concluded that in the equilibrium solution more ions were taken into account in the calculations than their number determined by measurement.

TABLE 4·

HCl adsorption of clinoptilolite from HCl-solution

Activated sorbent	Initial solution concentration, HCl mmol/l	Concentration from initial conductivity on the basis of calibration, mmol/l	Specific conductivity of the solution, μS		Concentration of the equilibrum solution mmol/l	Adsorbed HCl, mmol	Adsorbed HCl, specific mmol/100 g sorbent	Duration of measurement (hour)
			initial solution	equilibrium solution				
1	2	3	4	5	6	7	8	9
clinosorb	2.0	2.09	838	735	1.86	$1.84 \cdot 10^{-2}$		1.1
clinosorb	2.0	2.09	838	539	1.41	$5.44 \cdot 10^{-2}$		7.7
clinosorb	2.0	2.09	838	669	1.70	$3.12 \cdot 10^{-2}$	3.28	8.3
clinoptilolite	2.0	2.09	838	713	1.82	$2.16 \cdot 10^{-2}$	2.20	26.8

On this basis it could not be decided that from the solution the ammonium, hydrogen resp. chloride ions were adsorbed on the surface of the sorbent in such an extent which surpassed the ion exchange capacity. To study this problem two kinds of investigations were performed. On the one hand, activated clinosorb and clinoptilolite were taken into a solution of hydrochloric acid the concentration of which was nearly the same than that of the ammonium chloride used in the experiments

and then the conductivity of the hydrochloric acid solution was measured till the equilibrium reached. It can be seen from the data of Table 4 that the conductivity of the hydrochloric acid solutions taken in interaction with the sorbents has decreased. Consequently, ions originating from the solution were bound in the surface of the sorbents which relates to adsorption, since the sorbents contained the same number of cations as contra-ions and ion exchange could not be taken into account.

In the other type of investigations activated clinoptilolite was put into ammo-

TABLE 5

Ion exchange and adsorption of ammonium hydroxide on clinoptilolite in diluted solution

Activated sorbent	Solution concentration NH_4OH mmol/l		Specific sorbed NH_4^+ mmol/100 g	Concentration of the solution after flushing mmol/l	Flushed NH_4OH mmol	NH_4^+ remained on the sorbent after flushing, mmol/100 g sorbent	Flushed NH_4OH, mmol/100 g sorbent
	initial	equilibrium					
1	2	3	4	5	6	7	8
clinosorb	1.98	0.025	16.07				
clinoptilolite	1.98	0.02	15,84				
clinosorb	4.49	0.22	33.44	0.0858	$6.8 \cdot 10^{-3}$	32.76	0.68
clinosorb	6.07	1.54	36.43	0.3428	$27.4 \cdot 10^{-3}$	33.68	2.75

nium hydroxide solution of different concentration and the specific conductivity values of the equilibrium solutions were measured, further the change of ammonium ion concentration of these solutions was determined. The concentration of the most diluted ammonium hydroxide solution agreed with that of the ammonium chloride used in the experiments.

Data of Table 5 summing up the results of these experiments show that the greater was the concentration of the starting ammonium hydroxide the greater was the adsorbed ammonium quantity.

Separating the sorbents from the equilibrium solutions by decanting and flushing them twice in 5—5 ml distilled water, the sorbents were put into 80—80 ml ion-free distilled water and the conductivity of the solutions of equilibrium as well as the quantity of the ammonium ions getting the solution were measured. Regarding the fact that the water being in interaction with the sorbents did not contain contra-ion, only adsorbed ammonium could get the solution (in addition to the exchange capacity).

It is obvious from the data of the Table that independently of the concentration of the ammonium hydroxide solution, after flushing always the ammonium ion quantity corresponding to the ion exchange capacity remained and the ammonium quantity over the ion exchange capacity got the solution. The quantity of this, however, increased with the increasing starting concentration of the ammonium hydroxide solutions contacting the clinoptilolite.

On this basis it is expected that in the sorbents taken in interaction with solutions containing ammonium ions the ion exchange and adsorption may form simultaneously. The ratio of ion exchange and adsorption, however, is the function of the concentrations of the starting solutions. When these solutions contain contra-ions corresponding to only the ion exchange capacity, only the ion exchange should be taken into

account, since the energy of valence of this process is greater than the adsorption of the ion in question.

It is exactly demonstrated in Tables 4 and 5 that from the hydrochloric acid and ammonium hydroxide solutions of same concentration the measure of specific adsorption is also the same.

The mineralogical data of the clinoptilolite-bearing rock showed that in addition to clinoptilolite other accessorial minerals are also present which do not possess ion exchange character but they are able to adsorb different ions. On this basis it is plausible that the measure of ion exchange is the function of clinoptilolite content, while adsorption depends on the quantitative ratio of the other accessories having sorption capacity. Thus, the applied electrochemical method may be suitable to characterize the surficial features, resp. zeolite content of the zeolite-bearing rocks having ion exchange possibilities.

SUMMARY

The mineralogical and sorption features of the clinoptilolite-bearing rocks of the Tokaj Mountains were investigated. On the basis of X-ray diffractometric, infrared spectroscopic and chemical analyses the qualitative and quantitative composition of the rock was determined, further the water content of the clinoptilolite was characterized. On the basis of electrochemical investigations (joint measurement of conductivity and potential) it was stated that the rock possesses ion exchange and adsorption features. The ion exchange capacity proved to be 0.33 mval/g. The adsorption capacity is a function of the concentration of the solution being in interaction with the rock.

The applied electrochemical method seems to be suitable to characterize the surficial features, resp. zeolite content of the zeolitized pyroclastics of ion exchange capacity.

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NEWER LIME-SECRETING ALGAE FROM THE MIDDLE CARBONIFEROUS OF THE BÜKK MOUNTAINS, NORTHERN HUNGARY

M. NÉMETH

INTRODUCTION

It was recognized during geological excursions in the Bükk Mountains that certain limestone lenses of the Upper Moscovian shale sequence yield other calcareous algae than those *dasycladaceans* (*Vermiporella* sp., *Anthracoporella* sp., *A. spectabilis* PIA and *Dvinella comata* CHVOROVA) described previously by HERAK, M. and KOCHANSKY, V. [1963]. From limestone samples came from the No. 1 railway cutting of Nagyvisnyó, from the eastern side of the Bánvölgy (NW to the Dédes Castle), from the southern vicinity of the village Mályinka, from Kapubérc, from western side of the summit of Tarófő and from deeper part of the main lens of Nagyberenás the forms of the genera *Archaeolithophyllum, Ivanovia, Oligoporella*? and *Osagia* have been recognized. The first two genera belong into the phylloid algae of PRAY, L. C. and WRAY, J. L. [1963]. The genus *Macroporella* is classed among the family *Dasycladaceae*, while the *Osagia* is a crustose calcareous alga of uncertain systematic position.

Most interesting are the *phylloid algae*, which are similar in shape and size to leaves and are slightly or strongerly wavy. In spite of the morphological similarity that suggested by their common name, these are forms of different groups (e.g. green or red algae). This group was named by American authors, because these *phylloid algae* are abundant, occasionally in rock-forming quantity in the Middle and Upper Carboniferous (Pennsylvanian) and Lower Permian of the USA. On the other hand, the preservation of the cavities between the wavy plates of these algae promotes significantly the formation of hydrocarbon traps within the embedding rocks. This group thoroughly treated also in the Soviet Union, e. g. the description of the genus *Ivanovia* was given by CHVOROVA, I. V. [1946].

The present paper, besides of the summarization of this group hitherto unknown in Hungary, widens the knowledges about the geographical distribution of these forms.

CHARACTERIZATION OF THE EMBEDDING STRATA

The Upper Moscovian, 5 to 50 m thick limestone lenses of the Bükk Mountains consist of dark-grey, locally brownish or brownish to light-grey, stratified limestones. The steeply dipping lenses, which are interrupted by dark shale beds, generally form parallel lines. At the above mentioned localities, on the weathered surfaces of the limestone beds, the thicker or thinner, slightly or strongerly wavy, simple or branching pattern of the lim-secreting algae is easily recognizable, because the

sparitic infilling of the internal cavities of the algal tubes and plates is rather resistant to the weathering as compared to the micritic or micro-sparitic matrix. The algae significantly facilitated the formation of the limestone lenses, by the following causes:

a) the connected pieces of the vertically growing forms — which are fastened together by crustose forms — supply a rigid fabric to the rock;
b) the fine calcareous mud, which formed from the broken and disintegrated parts of the wave-fragmented algae, supports the quantity of the sediment;
c) the vertically growing forms — by slowing the water agitation down — promote the in situ deposition of the calcareous mud.

On the basis of recent similarities, the environment of the algae was probably the shallow water. *Lithophyllum*, the recent equivalent of the *Archaeolithophyllum* habitates mainly the littoral zone [WRAY, J. L. 1964], but in the sublittoral zone, to the depth of 30 m, also can be found. An other possibility is that the phylloid algal colonies developed on the topographic heights of the former sea-floor, because the transillumination was more favourable here.

In the samples the position of the phylloid algal thalli shows a slight orientation (Plate II, *Fig. 1*), suggesting probably the smuggle of the algal plates to the sedimentation surface. On the other hand, this feature shows a slight water agitation, which would caused by the algal mat itself.

The fossil material of the studied samples — excepted the ones came from the deeper part of the main lens of Nagyberenás — yielded almost exclusively *Archaeolithophyllum* and *Ivanovia* specimens, and additional forms are smaller *foraminifers* and *crinoidal* ossicles. The representatives of the genera *Ivanovia* and *Archaeolithophyllum* are associated in the No. 1 railway cutting of Nagyvisnyó, but enrich in different parts of the limestone lens. This monotonity of the fossil content suggests that the algal mat of decreased water agitation did not favoure the proper life environment for other benthonic organisms.

On the other hand, the main lens of Nagyberenás suggests a more favourable environment with stronger agitation and increased food-supply, because besides of the rarer *Archaeolithophyllum* and *Ivanovia, Oligoporella?* sp., *Osagia* sp., *Bradyina* sp. (Foraminifera), some *Chaetetes* (tabulate coral) colony fragment, *gastropod* sections and *crinoidal* ossicles also can be found.

Because of the considerable recrystallization of the phylloid algal fossils of the Bükk Mountains, it was hard to range these remains into the proper ones of the four most important phylloid algal genera (*Anchicodium* JOHNSON, 1946; *Archaeolithophyllum* JOHNSON, 1956; *Eugonophyllum* KONISHI et WRAY, 1961 and *Ivanovia* CHVOROVA, 1946). Similar was the case with the recently found *Oligoporella?* sp. and *Osagia* sp. forms. In spite of the broader determinations used here, the author hopes that the following descriptions will convincingly record the Hungarian occurrence of these algal genera.

PHYLUM: Chlorophycophyta PAPENFUSS, 1946
Class: CHLOROPHYCEAE KÜTZING, 1843

Family: DASYCLADACEAE

Genus: *Oligoporella* PIA, 1912
Genotype: *O. pilosa* PIA

Oligoporella? sp.
PLATE I, Figs. 1—4

Description: Thallus cylindrical, central stem relatively thick. Open pores situating at different intervals form rather irregular whorls, nearly perpendicular to the central stem. Diameter of the thallus (D) 1,1 to 1,5 mm, wall-thickness (d) 0,13 to 0,30 mm, pore diameter (p) 0,11 to 0,16 mm.
Remarks: Paleozoic forms assigned to the genus *Oligoporella* have been recorded mainly from the Permian of Japan (JOHNSON, J. H. 1963, p. 177). But the Japanese Upper Pennsylvanian *Oligoporella* sp. — is rather a *Macroporella.* Unfortunately the specimen number and the preservation of the hitherto available specimens from the Bükk Mountains unable a closer determination, but it is probably a new species.

Locality: Deeper part of the main lens of Nagyberenás.
Age: Upper Moscovian — Permian — Triassic.
Distribution: USA; Europe; Japan (for the genus).

Family: CODIACEAE (TREVISAN) ZANARDINI, 1843
Genus: *Ivanovia* CHVOROVA, 1946
Genotype: *I. tenuissima* CHVOROVA (1946, pp. 737—739, *Figs. 1—2*)

Ivanova sp.
PLATE II, Figs. 1—3
1963. *Ivanovia* sp.—JOHNSON,
pp. 23—24; PLATE 20, Fig. 3

Description: Slightly or strongerly wavy plates resembling leaves in shape and size, with 1 to 3 mm thickness in the Bükk Mountains' specimens and 1 to 1,5 mm thickness in general. The plates have a three-layered structure, i.e. the central medulla is bordered by two thinner cortex. On the basis of the comparison to the related genus *Anchicodium*, the medulla was presumably made up of mass of threads with non-calcified walls. Hence the original structure of the medulla is non visible on the available specimens; this is substituted sparitic or microsparitic infilling.
Remarks: The basis for the separation of this genus from the related genera of this same family is the mode of development of the originally calcareous cortex. According to KONISHI, K. and WRAY, J. L. [1961], on the basis of the cortic structure, these genera can be ragned into the phylogenetic lineage shown here in *Fig. 1.* The initial member of this lineage is the still crustless *Calcifolium*, the next members are the *Ivanovia* and *Anchicodium*, characterized by dark columnar and light triangular crustal parts, respectively. The endform is the *Eugonophyllum*, which shows a "double" crustal structure, uniting practically the features of the previous members *(Fig. 1*, Plate I, *Fig. 3).*

On the other hand, owing usually to the state of preservation, among these above mentioned three genera only the determination of the *Eugonophyllum* is possible on the basis of *merely the crustal structure studies.* As it was emphasized by JOHNSON, J. H. [1963], to make distinction between the genera *Anchicodium* and *Ivanovia* is doubtful enough. Therefore, besides the crustal structure, the shape of the thallus should also be take into consideration. Namely the *Anchicodium* is re-

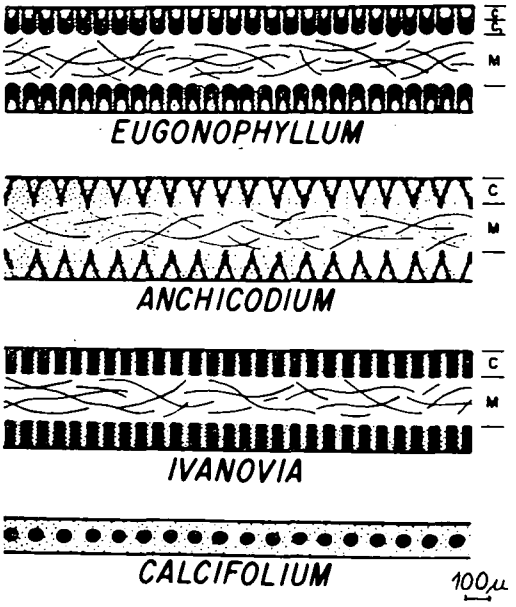


Fig. 1. Schematic diagram illustrating wall structures and phylogenetic progression of the Late Paleozoic phylloid *Codiaceae* after KONISHI, K.—WRAY, J. L. [1961. Degree of primary calcification is indicated by density of dotting. Inner part shot with filaments=medulla; that is bordered by cortex. (*Calcifolium* has yet no cortex.)

garded by JOHNSON, J. H. [1946, 1963] as a branching, cylindrical form (Plate I, *Fig. 4*), and the *Ivanovia* is characterized by CHVOROVA I. V. [1946] as a definitely plate form (see Plate I, *Fig. 5*). However, recent studies [*in* KONISHI, K. and WRAY, J. L. 1961] suggest a possible laminar thallus of certain *Anchicodium* species.

Accepting the conclusions of JOHNSON, the Bükk Mountains' specimens should be placed into the *Ivanovia*, because these are laminar and non-branching forms. This seems to be confirmed by the fact that the specimens do not show primarily calcified medullae and visible internal structure, similarly as in other *Ivanovia* forms known previously from the literature. On the other hand, the medulla of the *Anchicodium* retains the traces of the primary filamentous structure *(Fig. 1,* Plate I, *Fig. 4).*

The *Ivanovia* specimens of the Bükk Mountains are generally two or three times thicker as the 0,5 mm thickness recorded by CHVOROVA for the species *Ivanovia tenuissima.* Their micritic crust is hardly separable from the similarly micritic matrix. However, the characteristic columnal structure of the cortex — in spite of the considerable recrystallization — is recognizable in some cases (Plate II, *Figs. 2—3*). The lenght of the small micritic columnals inserting the sparitic medulla is about 0,08—0,10 mm. However, this feature do not allow specific identification.

Localities: Eastern side of the Bánvölgy (NW to the Dédes Castle); deeper part of the main lens of Nagyberenás; No. 1 railway cutting of Nagyvisnyó (7/1955. P. SZABÓ); western side of the summit of Tarófő.

Distribution: This genus has been recorded from the Moscow Basin, from the USA and Yugoslavia sor far.

Age: Middle Carboniferous — lower part of the Upper Carboniferous (Atokan — Des Moinesian — Missourian). In Hungary: Upper Moscovian.

PHYLUM: RHODOPHYCOPHYTA PAPENFUSS, 1946

CLASS: RHODOPHYCEAE RUPRECHT, 1851

Family: CORALLINACEAE or SOLENOPORACEAE

Genus: *Archaeolithophyllum* JOHNSON, 1956

Genotype: *A. missouriense* JOHNSON

Archaeolithophyllum cf. *missouriense* JOHNSON

PLATE IV, *Figs. 1—5*

1963. *Archaeolithophyllum missouriensum* — JOHNSON, pp. 6—7; PLATE 2, *Figs. 1—2;* PLATE 3, *Fig. 2*

1964. *Archaeolithophyllum missouriense* — WRAY, pp. 7—8; text-*figs. 3—4;* PLATE 1, *Figs. 1* and *3—7*

1964. *Archaeolithophyllum missouriensum* — KOCHANSKY-DEVIDÉ p. 516; PLATE III, *Fig. 1*

Description: By the original description the thallus is irregular, strongly wavy plate or crust of variable thickness, with common small protuberances (Plate II, *Fig. 4*). On the transversal sections of extremely well preserved specimens the three-layered thallus is visible (Plate III, *Fig. 1*). The thicker central hypothallus, wich is formed curved lines of larger, polygonal cells is covered on the one or both sides by the thinner perithallus consisting of smaller, rectangular cell-layers parallel to the surface. The first case suggests crustose, the second partially attached, non-crustose forms. Sporangia were situated in conceptacles (Plate III, *Figs. 2—3).*

The shape of the specimens from the Bükk Mts. agree well with this characterization. The thickness of the strongly wavy blades is 0,1 to 0,8 mm, the order of magnitude of the protuberances on the plates (Plate IV, *Fig. 4*) is 0,1 mm. The peri- and hypothallus are somewhat distinct, but their internal structure — because of the recrystallization — usually cannot be studied. The hypothallus is replaced by sparitic or microsparitic material (Plate IV, *Fig. 1*). Algal fragments retaining the traces of the original cellular structure are very rare (Plate IV, *Fig. 2*). In some cases, however, even the conceptacles are visible too (Plate IV, *Fig. 5*).

Remarks: The specimens from the Bükk Mountains are identical in shape to the species *Archaeolithophyllum missouriense* JOHNSON; these are symmetrical, i. e. non-crustose forms. Although the diameter of the conceptacles is significantly smaller (100—230 μ) than that of given by JOHNSON, J. H. (585—990 μ), their shape show closest resemblance to the *A. missouriense* from the hitherto known non-crustose *Archaeolithophyllum* species.

PLATE I

1—2. *Oligoporella* ? sp. — Deeper part of the main lens of Nagyberenás. 5/1970. B. K. Bükk Mts. — Upper Moscovian.
1. Slightly oblique longtudinal section. *2.* Slightly oblique cross section.

3. *Eugonophyllum johnsoni* KONISHI et WRAY. Transversal section in slide, with a well-kept cortical structure. — Holder formation, Otero County, New Mexico, USA. — After KONISHI, K.—WRAY, J. L. [1961] and JOHNSON, J. H. [1963, Plate 18, Fig. 8.]
4. *Anchicodium funile* JOHNSON, in thin section. — Wakarusa limestone, Brown County, Kansas, USA. — Late Pennsylvanian. — After JOHNSON, J. H. [1946, Plate 7, Fig. 1 and 1963, Plate 17, Fig. 4].
5. *Ivanovia* sp. Nearly transversal section in slide. — Hermosa formation, New Mexico, USA. — Pennsylvanian. — After JOHNSON, J. H. [1963, Plate 20, Fig. 3].

PLATE II

1. *Ivanovia* sp. Polished surface. — Western side of the summit of Tarófő. Collected by F. LEGÁNYI. Bükk Mts. — Upper Moscovian.

2—3. *Ivanovia* sp. Transversal section in slide, with spoors of columnar structure of the cortex (arrows). — Nagyvisnyó. Western side of the railway cutting No. 1 Bükks Mts. — Upper Moscovian.

4. *Archaeolithophyllum missouriense* JOHNSON. Polished surface. — Captain Creek limestone, Wilson County, Kansas, USA, — Pennsylvanian. — After WRAY, J. L. [1964].

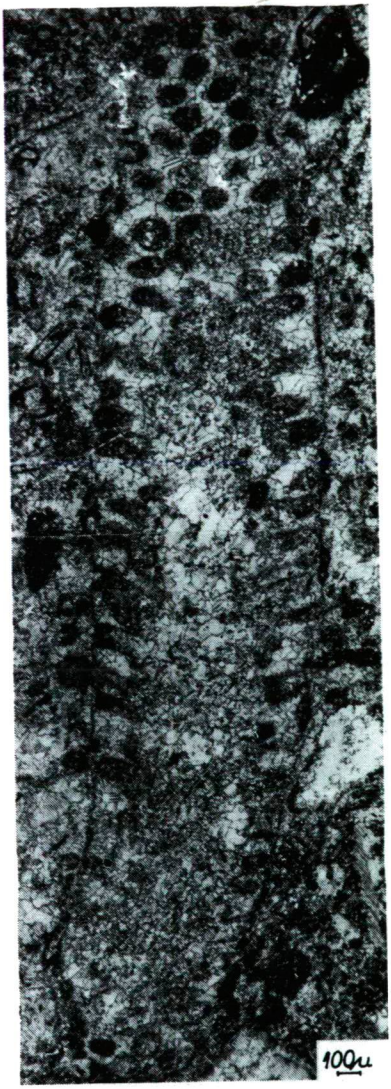
PLATE III

1. *Archaeolithophyllum missouriense* JOHNSON. Transversal section in slide. — *h:* hypothallium, *p:* perithallium. — Collinsville, Illinois, USA. — Pennsylvanian. — After JOHNSON, J. H. [1956, Plate 14, Fig. 3].
2. *Archaolithophyllum delicatum* JOHNSON. Highly arched conceptacle in slide. — Collinsville limestone, Collinsville, Madison County, Illinois, USA. — Pennsylvanian. — After JOHNSON, J. H. [1956, Plate 14, Fig. 6].
3. *Archaeolithophyllum missouriense* JOHNSON. Two conceptacles surrounded by perithallic tissue, in slide. — Carroll County, Missouri, USA. — Pennsylvanian. — After JOHNSON, J. H. [1956, Plate 14, Fig. 1].

PLATE IV

1. *Archaeolithophyllum* cf. *missouriense* JOHNSON. Thin section of a strongly recrystallized individual. — South of Mályinka, 450 m from Mártuskő in ENE direction. 52/1955. B. K. Bükk Mts. — Upper Moscovian.
2. *The same.* Thin section of a slightly recrystallized individual. — Deeper part of the main lens of Nagyberenás. 5/1970. B. K. Bükk Mts. — Upper Moscovian.
3. *The same.* Polished surface. — Nagyvisnyó. Railway cutting No. 1 Bükk Mts. — Upper Moscovian.
4. *The same,* with protuberances raised above body of the plant. Transversal section in slide. — Deeper part of the main lens of Nagyberenás. 5/1970. B. K. Bükk Mts. — Upper Moscovian.
5. *The same.* Image of a conceptacle in slide. — South of Mályinka, 450 m from Mártuskő in ENE direction. 52/1955. B. K. Bükk Mts. — Upper Moscovian.

6—7. *Osagia* sp. Thin section. — Deeper part of the main lens of Nagyberenás. 5/1970. B. K. Bükk Mts. — Upper Moscovian.



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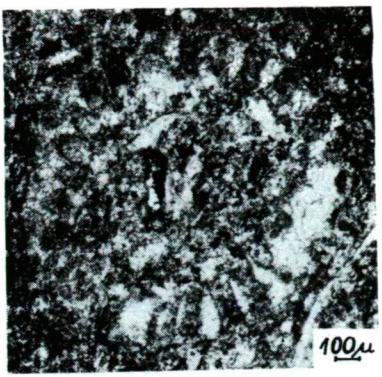

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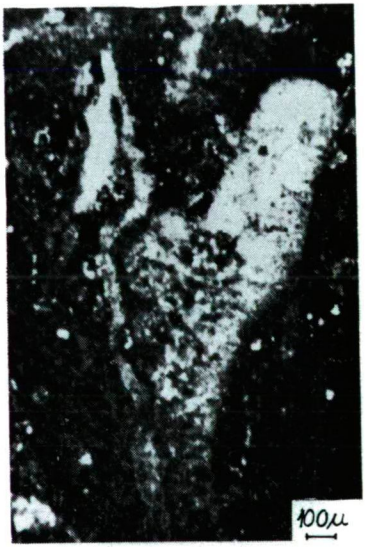

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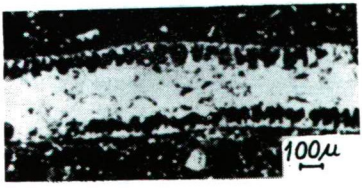

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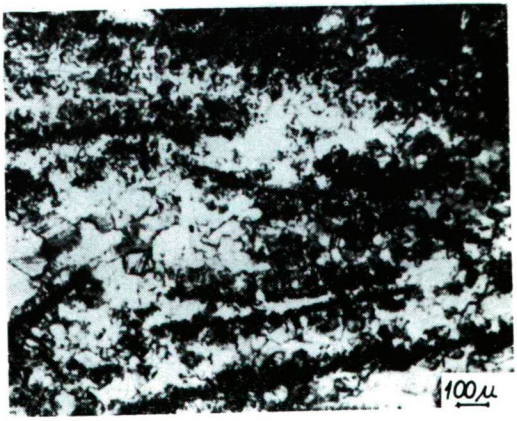

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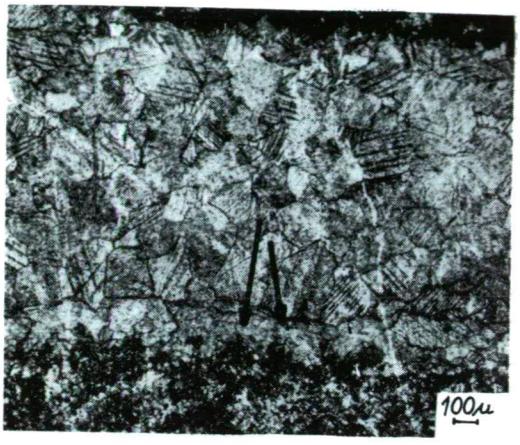

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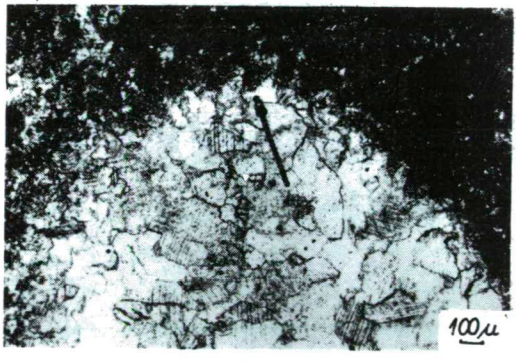

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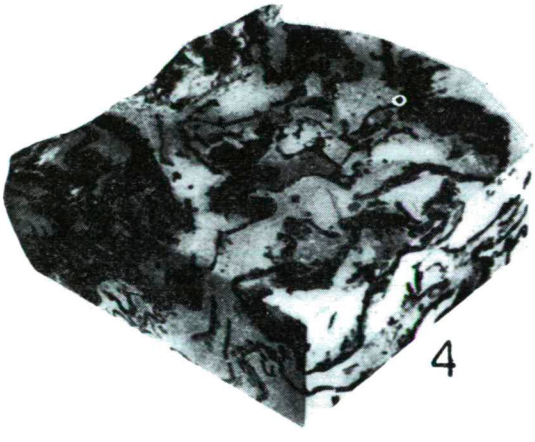

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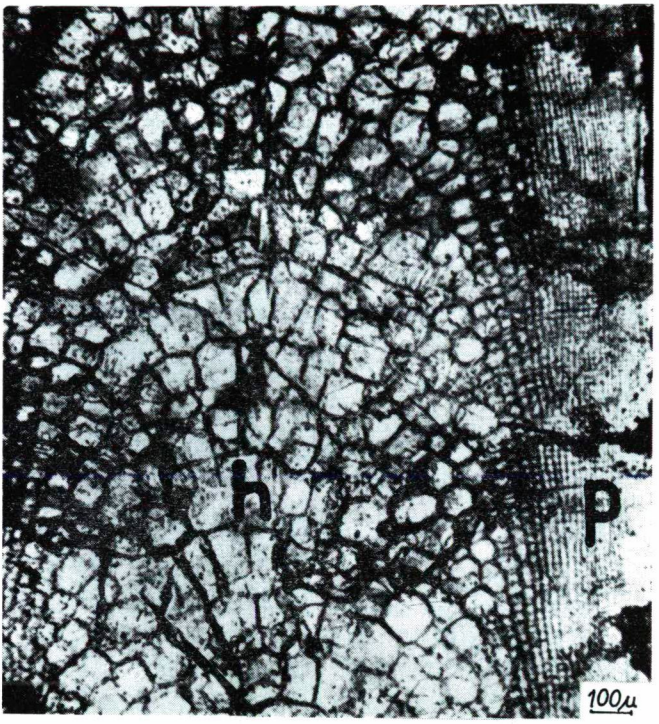

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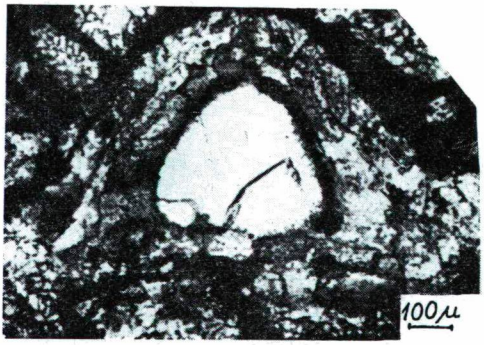

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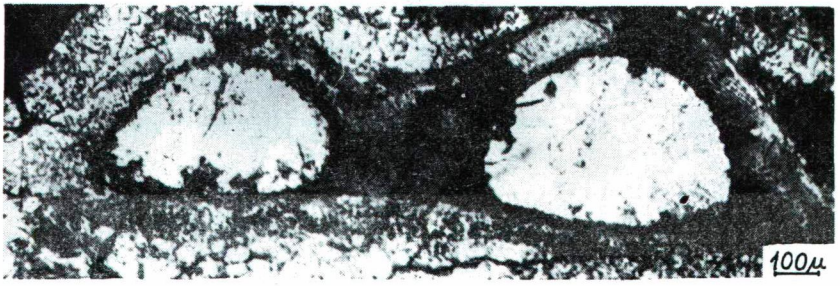
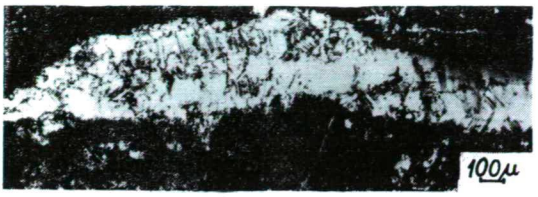
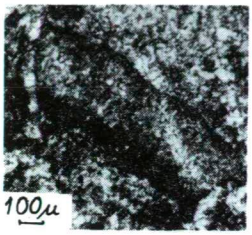



1
100μ


5
50μ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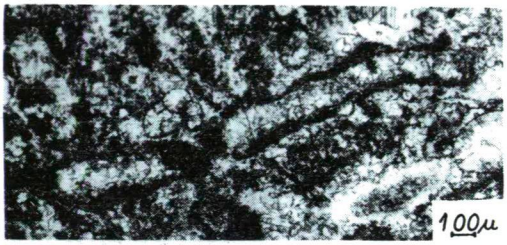
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3
5
4
3
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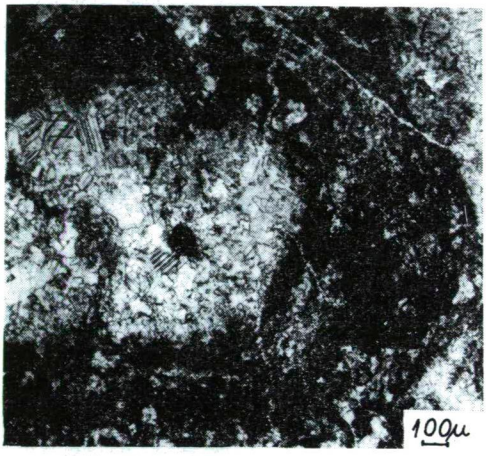
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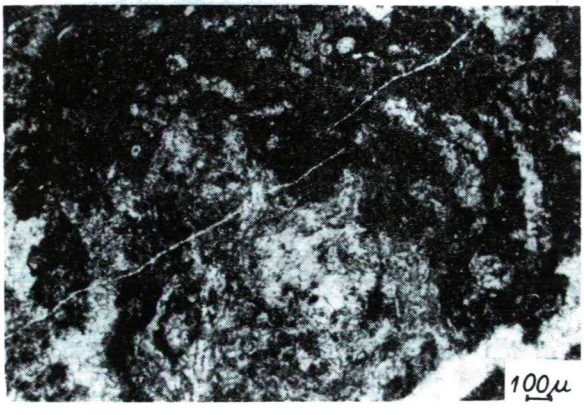
7
100μ

Localities: No. 1 railway curting of Nagyvisnyó; south to the village Mályinka, 450 m ENE Mártuskő (52/1955. B. K.); Kapubérc; deeper part of the main lens of Nagyberenás.
Distribution: USA; Karawanken (N to Jesenice); Velebite Mountains.)
Age: Upper part of the Middle Carboniferous — uppermost Carboniferous (as of genus: basal Middle Carboniferous to basal Lower Permian).

ALGAE INCERTAE SEDIS

Section Prostromata PIA, 1927

Genus *Osagia* TWENHOFEL, 1919

Genotype: *O. incrustata* TWENHOFEL

Osagia sp.

PLATE IV, *Figs. 6—7*

1946. *Osagia* sp. — JOHNSON, pp. 1102—1104; Plate 2, Figs. 3—5; Plate 4, Figs. 3—5; Plate 5, Figs. 5—6; Plate 10, Fig. 2

1963. *Osagia* sp. — JOHNSON, p. 27; Plate 22, Figs. 2—4

Description: Laminar thallus built up by light tubes and chambers, which are covered by dark, fine algal filaments. The thallus usually encrusts fossil fragments. The shape of the thallus around the internal core resembles corn or bean. In contrast to the largest thallus diameter (5,8 mm) found by JOHNSON, J. H. the main lens of Nagyberenás yielded thallus of 15 mm lenght. Because the thallus diameter depends also on the size of the encrusted fossil (in this case this is a phylloid alga fragment), hence even this measurement cannot be regarded as exceptional (Plate IV, Fig. 7).
Remarks: According to JOHNSON (loc. cit.) the *Osagia* thallus was formed by the symbiosis of filamentous algae similar to *Girvanella* and crustose *Nubecularia* foraminifers. Consequently this is rather a growth-form as an independent species.
Distribution: USA; Yugoslavia; Hungary.
Age: Middle Carboniferous — Lower Permian.

ACKNOWLEDGEMENT

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DETERMINATION OF THE METHOXY-GROUP CONTENT OF INSOLUBLE ORGANIC SUBSTANCES OF SEDIMENTS

M. BALOGI and M. VADKERTI TÓTH

INTRODUCTION

A major part of geochemical investigations carried out in connection with hydrocarbon occurrences aimed to decide whether the sediment is either a source rock of hydrocarbons or perhaps it is merely a resevoir-rock where the hydrocarbons accumulated by migration.

However, so far investigations of the identification of source-rocks have not yielded exact results. [MACOVEI, 1928; TRASK, 1932; TRASK and PATNODE, 1942; PHILIPPI, 1957; BRENNEMAN and SMITH, 1958; KALIFEH and LOUIS, 1961; BREGER and BROWN, 1962; HEDBERG, 1964; BRAY and EVANS, 1965. — cited by NAGY, B. and U. COLOMBO, 1967.]

Relying upon results obtained through experiments of investigators referred to, COLOMBO [1967] stated that practically it is impossible to draw a well defined line between hypothetical source-rocks and no-source ones. This statement means that all sedimentary rocks more or less contribute to the generation of hydrocarbons, which at last are accumulated in the reservoir rocks.

To decide to what extent had the organic matter coming from a given area contributed to the formation of hydrocarbons found there, very important data may be yielded by a complex study of kerogen, the insoluble organic material of sediments.

FORSMAN and HUNT [1958] differentiate three types of kerogens isolated from sediments coming from different localities. They classify coaly-, non-coaly oil shale- and coaly oil shale-types.

Coaly-type kerogens are very markedly similar to substances found in peat, lignite and other coals; they mostly consist of lignin-like compounds. These kerogens can be regarded as built up of macromolecules consisting of condensed aromatic rings, wherein the rings are connected by ether-, alkoxi- and sulphuric bridges, respectively. Hydroxyl-, methoxy- and sometimes esterified carboxyl-groups may be connected with the aromatic core.

Non-coaly oil shale kerogens are characterized by straight-chain structures, with little cycloparaffin and an aromatic ring with one core, connected with a functional group with less oxygen content.

Coaly oil shale kerogens, as regarding their properties represent a transition between kerogens classified in the former two types.

It has been pointed out that from the point of view of the formation of hydrocarbons sediments containing non-coaly oil shale kerogens are the most important.

A number of experiments have been carried out to classify kerogens of sediments of different hydrocarbon occurrences according to the former classification.

These experiments had as a primary aim to isolate from the rocks, to determine the composition and to clear up the structure of kerogens.

Besides the above mentioned studies some important data could be obtained by determining the periferical functional groups, what is a well-known method in the case of different carbons. However, literature contains relatively few data on kerogen. [SEMENOV *et al.* 1955; VAN KREVELEN and SCHUYER, 1957; AARNA and LIPPMAA, 1957. — cited by A. S. FOMINA *et al.*, 1965.]

Especially important data may be got by the determination of the methoxy-group content, since from this deductions can be made on the type of the kerogen isolated from the sediment, its being of coaly-type or non-coaly oil shale type, and whether it might have played a role in the formation of hydrocarbons. [FORSMAN, 1963.]

Having this problem cleared up may help in marking the direction of possible migration, discovering further hydrocarbon occurrences.

The subject of the present study is how to make applicable the determination of the methoxy-group content, a generally used method, for the study of insoluble organic-carbon content of sediments.

EXPERIMENTAL PART

For the analytical determination of the periferic methoxy-group content of kerogen essentially we have used a modified version of the hydrogen iodide acid method described by ZEISEL [1885].

The essence of ZEISEL's method can be summarized as follows: periferic methoxy-groups react with hydrogen iodide forming methyl-iodide:

$$R-OCH_3+HI \rightarrow R-OH+CH_3I$$

Methyl-iodide formed in an equivalent to the methoxy-groups amount has a lower boiling point thus it easly can be expelled from the system by heating. The formed methyl-iodide vapours are adsorbed by bromine dissolved in glacial acetic sodium acetate:

$$CH_3-I+Br_2 \rightarrow CH_3-Br+Br-I$$

Bromine-iodide is formed, which, affected by excess bromine in aqueous media is oxidized to iodic acid

$$Br-I+2\,Br_2 \rightarrow HIO_3+5\,HBr$$

Excess bromine can be reduced by formic acid what is indicated by the solution loosing its colour:

$$Br_2+HCOOH \rightarrow CO_2+2\,HBr$$

Finally iodine formed in an amount equivalent to iodic acid can be determined with iodometry.

In order to make ZEISEL's method suitable for the determination of the methoxy-group content of insoluble organic substances of sediments, several modifications are necessary both regarding the apparatus and various steps of the method. *E. g.* in contrast to the description in the literature of introducing hydroiodide acid, it is better to add it dropwise through a funnel while cooling the reaction vessel to avoid the loss of methyl-iodide owing to a very rapid reaction; because of the slow gas stream the aqueous suspension of red phosphorus as a washing agent did not prove

to be suitable, therefore a 1:1 mixture of 5% sodium thiosulphate and 5% cadmium sulphate solutions was used taking much care that the temperature of the washing agent did not rise markedly otherwise the formation of sulphur from the decomposition of sodium thiosulphate would hardly affect the determination, etc.

To perform the determination the following apparatus was used *(Fig. 1)*.

The dissolution of 30—50 mg kerogen of <60 nm grain size measured in the reaction vessel was done by adding 0,5 g crystalline phenol, 0,2 g red phosphorus

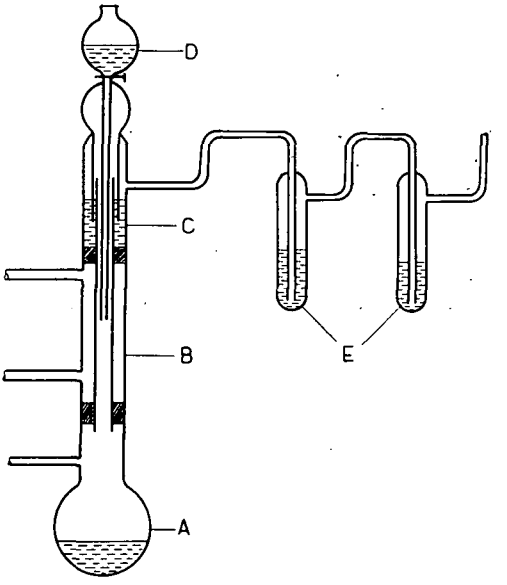

Fig. 1. An apparatus for the determination of the methoxy-group. A — reaction vessel; B — cooler; C — washer; D — funnel; E — absorption bulb

and 1 ml acetic acid anhydride, or propionic acid anhydride, under nitrogen atmosphere, then while cooling the reaction vessel, 5 ml hydrogen iodide, freshly distilled from red phosphorus was added dropwise from the funnel. Having this completed, the reaction vessel was heated to 140—150 °C by putting it in glycerin bath and maintaining this temperature for about two hours, the periferic methoxy-groups were transformed into methyl-iodide. The formed methyl-iodide vapours were led through a cooler — which is advisable to be heated only in the first third of the time of reaction — in 1:1 mixture of 5% sodium thiosulphate and cadmium sulfphate or the aqueous suspension of red phosphorus, and adsorbed in 10% sodium-acetate containing 10—12 drops of bromine, distributed in a one third-two thirds ratio in two parts of the adsorbing vessel. After the completion of the reaction the content of the adsorbing vessel is washed into an Erlenmeyer flask with a ground cork, a few drops of formic acid added to make the excess bromine react then, by adding 10 ml 2 N sulphuric acid and 0,5 g KI, after five minutes the iodine obtained is titrated with 0,1 sodium thiosulphate. The same process is used with the blank as well.

RESULTS AND DISCUSSION

To control the reproducibility and applicability of the method, as well as for the purposes outlined in the introduction, the methoxy-group content of non-coaly oil shale type kerogen, enriched from shale of brown coal and kukersite from Estonia, respectively, studied by other researchers as well was determined, then experiments were carried out with insoluble organic-carbon substances isolated from rocks deriving from the area investigated by us.

Values found in the literature compared with those measured and calculated by us are summarized in Table 1.

Although our aim was to develop a method suitable for an exact determination of the methoxy-group content of insoluble organic-carbon substances of kerogen and its sediments, respectively, on the basis of the obtained data we think that by the determination of the methoxy-group content of insoluble organic-carbon substances of kerogens of non-coaly oil shale type, coming from different localities and of sediments coming from our research area, some deductions can be made upon the properties of the latter samples. Deductions are to be made as well on the character of behaviour of the studied samples, which type can they be ascribed to, and accordingly, could they play a role in the formation of hydrocarbons, namely, the sediment studied is a mother rock or only a reservoir of the hydrocarbons found.

TABLE 1

Sample	Age	Locality	C W. %	$-OCH_3$ W. %		Notice
				Literary	Measured	
Lignin	—	—	68,18*	17,61*	—	*Calculated
Brown-coal	Pleistocene	Ecséd	54,4*	7,35*	7,25 7,32 7,38	*KEDVES and SIPOS [1967]
	Pleistocene	Gyöngyös-visonta	59,3*	8,75*	8,82 8,85 8,76	
	Miocene	Herend	56,9*	8,44*	8,48 8,56 8,50	
Kukersite-kerogen	Ordovician	Estonian SSR	66,65*	0,2*	0,21 0,30 0,25	*SEMENOV et al. [1955]
Isolated organic matter	Upper-Pannonian	Makó-7 S-100	31,52 73,57*	—	0,65 0,59 0,55	*Calculated on zero ash content
	Lower-Pannonian	Makó-2 S-111	22,35 64,04*	—	0,60 0,64	
	Lower-Pannonian	Makó-2 S-112	25,47 65,77*	—	0,48 0,52	

When determining by pyrolysis the degree of diagenesis of the insoluble organic content of the sediments, according to GRANSCH and EISMA [1966], in the case of the same type of organic matter, from the C_R/C_T quotient we can deduce on the degree of diagenesis; in the case of the same degree of diagenesis, on the type of the organic matter.

We think that the determination of the function groups and of those that of the methoxy-group may give further impact for the determination of the type of the organic matter.

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POSSIBILITIES OF CARBONATE CONTENT DETERMINATION OF SEDIMENTARY ROCKS

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INTRODUCTION

The determination of the carbonate content, or in narrower sense that of the quantity of the single carbonates of sedimentary rocks is of double aim. On the one hand this is necessary for the determination of the mineral composition of sedimentary rocks and for the characterization of a profile from the geochemical point of view, and it makes possible the determination of the quantities of Ca and Mg being in non-carbonate bond in the sedimentary rocks on the other. This latter is of special interest in the investigation of the evolution of the sediment.

Investigating the shales of the Russian platform VINOGRADOV and RONOV [1956, cited by VAN MOORT, 1973] observed the increase of Ca/Mg ratio from the Proterozoic towards the Tertiary. The same trend has been indicated by the shales of the North American platform [RONOV and MIGDISHOV, 1971, cited by VAN MOORT, 1973]. The older the rock, the higher Mg-content can be observed. The conclusions drawn from the data of chemical analyses were supported also by the results of investigations concerning the mineral composition, *i. e.* the carbonates of the older samples are dolomites while in the younger ones first of all calcite predominates. Having investigated the composition of the silicate fraction of carbonates of the sediments VAN MOORT [1973] observed the same trend of the Ca/Mg ratio though in the silicate fraction the absolute quantity of calcium and magnesium proved to be very low and the MgO-content shows an apparent decrease since the Paleozoic.

Out of the carbonate determination methods the simplest one resulting only informatory values is that used in the geological practice, in the course of which CO_2 is released from the sample by means of treatment with hydrochloric acid, whereas the cations form soluble chlorides. The CO_2 content can be determined from the weight loss following the release of CO_2 taking into account the reacting weights.

Numerous methods of carbonate determination are known, i. e. gasometric CO_2 determination, gravimetric CO_2 determination and the complexometric determination of Ca and Mg after acidic treatment, respectively. Any method, however, based on exact measurements is unable to produce the real quantities of calcite and dolomite when starting from the CO_2 content, at most informations can be obtained. The determination of the quantities of different carbonates may be problematic also in case of carbonate rocks. In case of sedimentary rocks where the carbonate content can vary within broad limits and the presence of numerous other minerals should also be taken into account, the determination of the CO_2-content is insufficient to that of the total carbonate quantity either. On the other hand, when the CaO and MgO content bound in silicate bond ought to be determined, this cannot be perform-

ed on the basis of the consideration that the carbonates will be dissolved by acidic treatment and in the acidic solution the CaO and MgO quantities being really in carbonate bonds are determined (and in this way the quantities being in silicate bond, too). This is unfeasible since in case of acidic treatment not only the carbonates are dissolved and not only the Ca, Mg and Fe contents of carbonates will be in the solution, but more or less other silicate minerals will also be dissolved, e. g. chlorite, first of all when dolomite of considerable quantity should be taken into account. In this case the major part of the carbonate phase does not dissolve in diluted acid without heating. Consequently, the solution will contain not only the carbonate minerals .

Thus, in case of more particular investigations other determination methods are needed.

To determine the quantitative relations of calcite and dolomite the X-ray diffractometric method is available. This is based upon the fact that using the records of standard mixtures and applying the calibration curves the ratio of the two carbonates mentioned above can be determined [TENNANT, BERGER, 1957].

In the cases when only the quantities of calcite and dolomite are to be determined, an other value should be taken into account for the determination of the absolute quantities of the two carbonates instead of their ratio. It seems to be practicable to connect the CO_2 determination to the X-ray diffractometric method.

In the paper of VAN MOORT quoted above the method initiated by GULDBRANDSEN [1960] is described and has been applied. We apply the method of TENNANT and BERGER [1957] for several years.

In the following a short review will be given that how reliable informations can be obtained regarding the calcite and dolomite content of the sedimentary rocks applying the X-ray diffractometric method together with the determination of the CO_2 content and with the investigation of the derivatograms concerning the carbonate content.

QUANTITATIVE DETERMINATION OF CALCITE AND DOLOMITE

Determination with X-ray diffractometer

The determination of the calcite/dolomite ratio can be performed by the method of internal standards [KLUG, ALEXANDER, 1954] which should be taken, however, with care since due to the mineralogical error only the calibration curve recorded from the samples of the area in question is suitable to the rapid and exact analysis of the minerals of the area. In case of samples deriving from other localities the analysis is less correct as a result of the mineralogical error.

When using the method of NÁRAY-SZABÓ and PÉTER [1964] the quantity of not only the carbonates but all the phases present in the sample can be determined on the basis of one record. It is disadvantageous, however, that in case of natural mineral mixtures which may contain considerable quantity of weakly crystallized minerals, moreover amorphous component, the application of this method may become problematic.

The absolute intensity of the strongest lines of calcite and dolomite is nearly 1:1 when their quantity is nearly the same in the sample. To determine this ratio the curve determined experimentally by TENNANT and BERGER [1957] can be applied. On the basis of the calibration curve the accuracy can be ± 5 per cent in case of 10 to 90 per cent dolomite content. The lower limit of identification is 2 to 3 per cent. DIEBOLD, LEMISCH and HILTROP [1963] obtained similar calibration curves.

Calibration series and preparation of the samples

To prepare the calibration series calcite from Parádsasvár and dolomite from Ratkószuha were used. Samples were powdered in agate grinding mill during a short time. The fractions of required grain size were separated by sedimentation. To make the calibration curves the fractions below 10 microns resp. between 10 and 30 microns were used. A calibration series of nine members were prepared from both fractions, the mixtures were mechanically homogenized so that no further change in grain size could follow. X-ray records were made with an X-ray diffractometer DRON—I, with Cu-radiation (30 kV, 20 mA). Detection was made by means of scintillation counter in front of which radiation has been monochromatized to $CuK_{\alpha 1}$. The rotation speed of the goniometer was 1/4° per minute.

To determine the percentual quantity of dolomite in the mixtures the intensity quotients of the strongest lines of 3.035 Å of calcite and of 2.886 Å of dolomite were counted and these were plotted as a function of the dolomite content of the mixtures of known composition.

The positions of the 104 reflexions as well as the ratios of peak-heights of the mixtures are summarized in Table 1. When plotting the values obtained in this way according to TENNANT and BERGER, the following calibration curves were obtained:

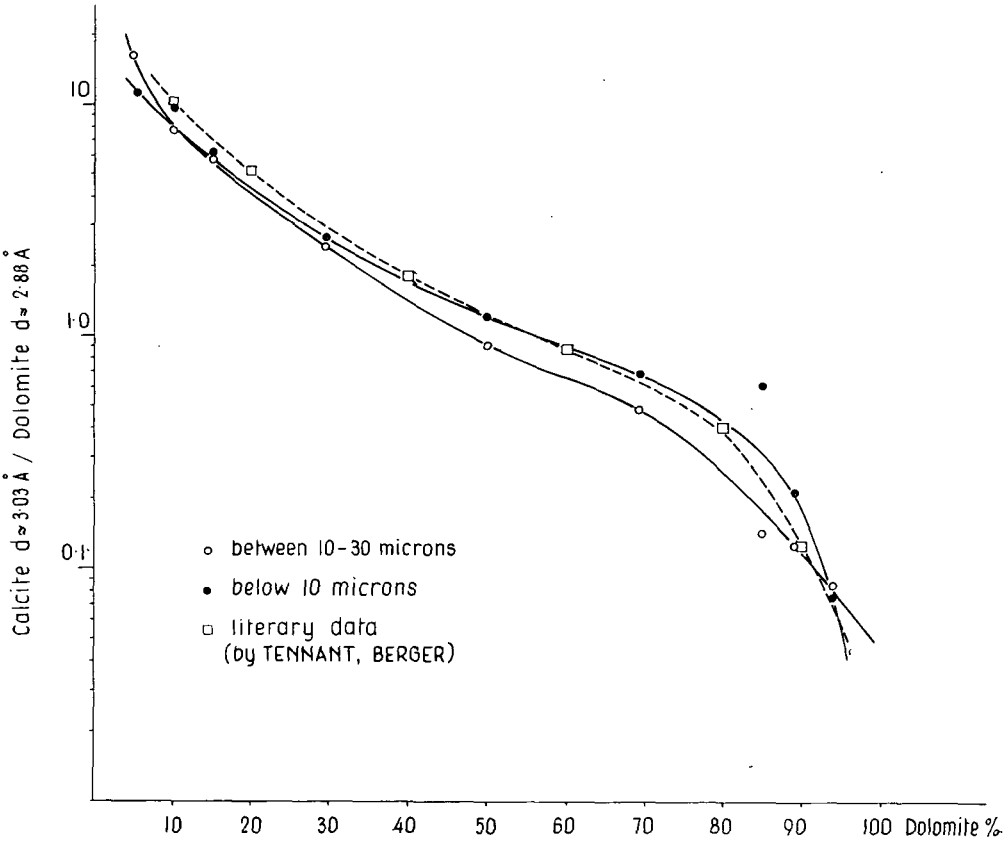

Fig. 1. Determination of calcite/dolomite ratio by means of intensity measurement of the strongest peaks of calcite and dolomite

The curves obtained are of the same shape than the calibration curve published by TENNANT and BERGER. In case of this demonstration, however, considerable subjective error can be introduced when plotting the curve, especially in case of the extreme values though these cases are most frequent in the investigated sedimentary rock samples. Thus we tried to introduce the plot of GULDBRANDSEN where

$$x = \log 100 \frac{\text{calcite \%}}{\text{dolomite \%}}; \qquad y = \log 100 \frac{\text{peak-height of calcite}}{\text{peak-height of dolomite}}$$

The data obtained in this way can be connected by a straight line. The plot can be made more precise when calculating the equation of the straight line from the measurements approximating most exactly them using the least square method. The following equations were obtained: to the fraction less than 10 microns $y = 0.4724 + 0.8253x$, to the fraction between 10 and 30 microns $y = 0.1154 + 0.9453x$. We tried to plot the data of the calibration curve published by TENNANT and BERGER also by this method and the calculated equation of the straight obtained in this way: $y = 0.1540 + 0.9713x$.

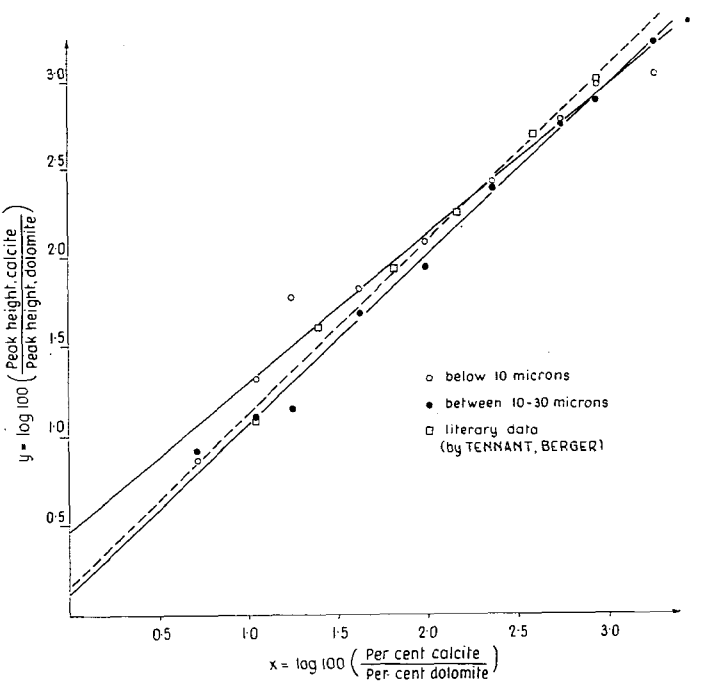

Fig. 2. Peak-height ratios of calcite to dolomite plotted against percentage ratios

The rise of the straight concerning the fraction between 10 and 30 microns approaches well that of the straight calculated from the data of TENNANT and BERGER, while that of the fraction below 10 microns is similar to the straight published by GULDBRANDSEN to the rocks of phosphate shales ($y = 0.3921 + 0.7885x$). The differences can be explained by those in localities and grain size.

Parallel with the X-ray diffractometric investigations the CaO, MgO and CO_2 contents of the mixtures were determined. The determination of the CaO and MgO

content was done by means of Komplexon III using Erichrom-Blue SE resp. Erichrom-black indicators. CO_2 was determined by means of gasometry. The prepared mixtures were of the following composition: calcite 55.92 per cent CaO and 43.84 per cent CO_2; dolomite 30.49 per cent CaO, 21.65 per cent MgO and 47,59 per cent CO_2. The calculated and measured compositions of the mixtures are shown in Table 2.

In the dolomite used for the mixtures the $CaCO_3/MgCO_3$ ratio proved to be 1.012 which hardly deviates from the stoichiometric composition.

The X-ray diffractometric method is favourable since by means of it really the calcite/dolomite ratio can be obtained. Knowing the calcite/dolomite ratio determined in this way and the CO_2 content the $CaCO_3$ and $CaMg(CO_3)_2$ contents of the samples can be determined. Subtracting these values from the total CaO and MgO contents the quantities of CaO and MgO bound in the silicates are obtained. This calculation, however, introduces another uncertainty because it supposes the presence of only calcium and magnesium in the carbonates though Fe(II) may also be present in carbonates. Further, when calculating the quantities of calcite and dolomite only calcite and Ca—Mg-dolomite of 1:1 ratio were taken into consideration though magnesium may be present in the calcite lattice without the presence of dolomite-phase and dolomite is not Ca—Mg-dolomite of 1:1 ratio, either, respectively. When the position of the 104 reflexion of calcite shows deviation from the literature data this fact relates to the built-in of $MgCO_3$ into the calcite lattice. Such Mg-calcite occurrences play predominant role mainly in recent marine sediments. The relation between the $MgCO_3$ content built-in in the calcite lattice and the position of the strongest calcite line (d = 3.036 Å) was investigated by GOLDSCHMIDT, GRAF and JOENSUU [1955] in case of Mg-containing calcites and by GOLDSCHMIDT and GRAF [1958] in case of Mg-containing synthetic calcite. When the position of the 104 reflexion of dolomite deviates from the literature value this always relates to the deviation from the stoichiometric composition of dolomite. When the $CaCO_3$ builts in into the lattice of dolomite the peak occurring at d = 2.886 Å follows at ever higher d-values [FÜCHTBAUER, GOLDSCHMIDT, 1965].

Thermal analyses

To control the mixtures the derivatograms of the grain size fraction of 10 to 30 microns were also recorded. In the course of our investigations the question should be answered that the decrease of weight being determinable by means of DTG and TG curves how accurately give the CO_2 content deriving from the thermal decomposition of carbonates. The losses of weight read off in the TG-curve and the CO_2 content determined gasometrically are summarized in Table 3. In the samples the average CO_2 content calculated on the basis of the TG-steps is 45.88 percent while the average value of the gasometrically determined CO_2 content proved to be 45.82 per cent. In case of investigation of 31 sedimentary rock samples the results showed similar agreement (10.59 per cent — by means of derivatograph, resp. 10.52 per cent by means of gasometry).

This really good agreement of the CO_2 contents determined by the two kinds of methods does not mean that in case of single samples considerable differences do occur; these, however, become equalized in case of averaging. The greater deviations can be explained by the fact that the beginning of the step indicating the thermal decomposition of carbonates is very difficult to be determined since in addition to the carbonates of the sedimentary rocks different phyllosilicates should also be taken into account the main endothermal effect of which just precedes the decomposition of the carbonates. Besides the mineral composition the grain size of carbonates is

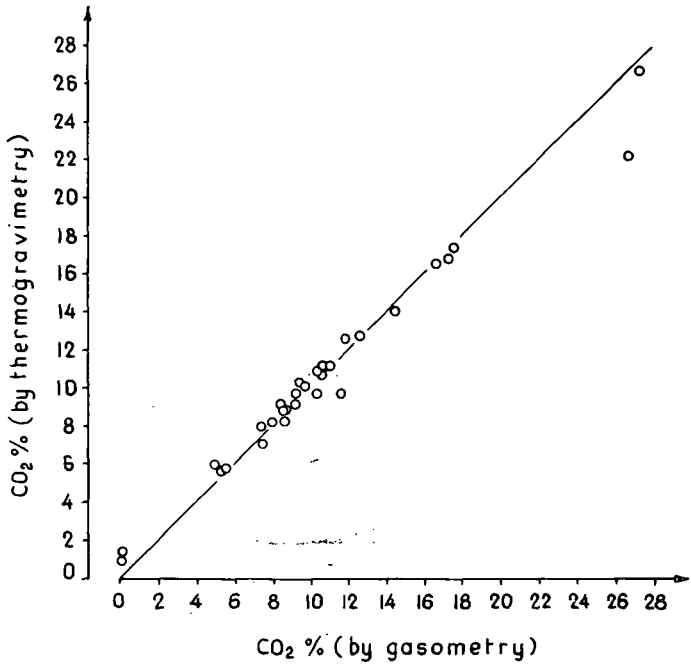

Fig. 3. Relation obtained by gasometric and derivatographic methods in the natural sedimentary rock samples

also influencing factor. When exact data are not required, the change of carbonate content *e. g.* as a function of depth can be characterized by the CO_2 content determined by derivatograph, in general.

The change of the endothermal peaks and of the temperatures of the inflexion point of the TG-curve are shown in Table 4.

The first endothermic peak about 780 °C showed only a fluctuation of about 2 to 3 °C when having changed the ratios of carbonates. The change of the second

TABLE 1

Grain size / Composition of the mixture	between 10 and 30 microns			below 10 microns		
	Calcite d_{104} Å	Dolomite d_{104} Å	$\frac{d_{3,035}\text{ Å}}{d_{2,886}\text{ Å}}$	Calcite d_{104} Å	Dolomite d_{104} Å	$\frac{d_{3,035}\text{ Å}}{d_{2,886}\text{ Å}}$
5% C+95% D	3,026	2,883	0,084	3,016	2,874	0,075
10% C+90% D	3,026	2,883	0,125	3,026	2,883	0,210
15% C+85% D	3,026	2,883	0,140	3,026	2,883	0,600
30% C+70% D	3,026	2,883	0,480	3,026	2,883	0,680
50% C+50% D	3,026	2,883	0,890	3,026	2,883	1,220
70% C+30% D	3,026	2,883	2,450	3,026	2,883	2,600
85% C+15% D	3,026	2,874	5,750	3,021	2,874	6,030
90% C+10% D	3,026	2,874	7,700	3,026	2,883	9,720
95% C+5% D	3,021	2,870	16,410	3,,021	2,874	11,050

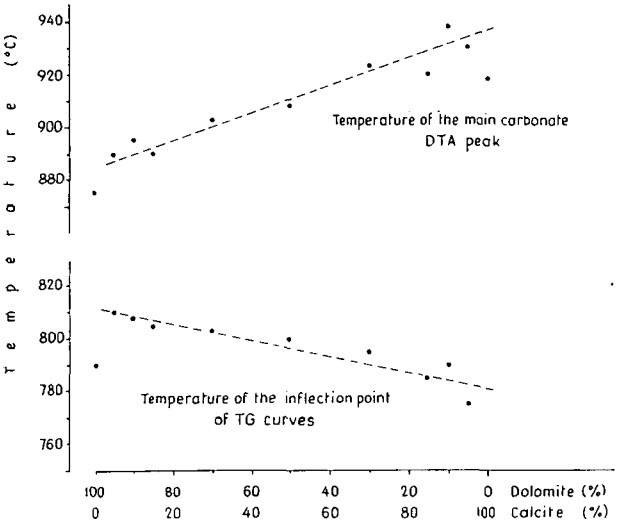

Fig. 4. Change of the second endothermal peak and of the temperature of inflexion of the TG-curve as a function of the composition of the mixture

endothermic peak, however, is more conspicuous, i. e. the more calcite contains the sample, it is displaced towards the higher value. On the TG-curve the temperature of the inflexion point shows a definite decrease with increasing calcite content though to a smaller extent.

The peak-temperature value of the endothermic main effect of carbonates are influenced by the grain size, the quantity as well as by the calcite to dolomite ratio. The lower is the grain size resp. the smaller is the total quantity of carbonates, the lower is the temperature of the endothermic main effect of the DTA curve. Similar

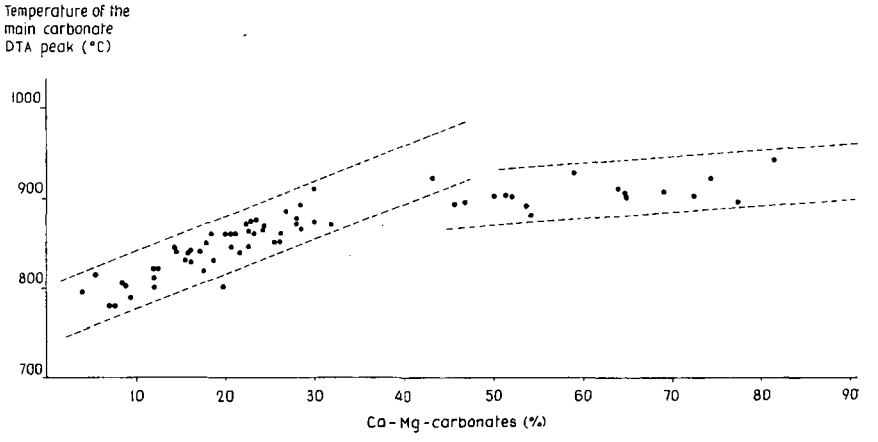

Fig. 5. Relation of the peak temperature of the carbonate endothermic main effect to the quantity of carbonates

TABLE 2

Mixture	Calculated composition			Measured composition					
				< 10 μm			Grain size 10—30 μm		
	CaO %	MgO %	CO_2 %	CaO %	MgO %	CO_2 %	CaO %	MgO %	CO_2 %
5% C+95% D	31,75	20,57	47,40	32,42	19,50	47,50	32,08	19,27	47,28
10% C+90% D	33,03	19,48	47,21	32,92	19,11	47,20	32,89	19,52	47,32
15% C+85% D	34,31	18,40	47,03	34,71	18,11	47,10	34,15	18,46	47,31
30% C+70% D	38,12	15,16	46,46	37,84	14,88	46,60	37,83	14,84	47,12
50% C+50% D	43,21	10,83	45,71	42,85	10,67	45,70	43,12	11,17	45,65
70% C+30% D	48,29	6,49	44,97	47,82	6,35	45,07	48,18	6,35	45,14
85% C+15% D	52,10	3,25	44,40	52,06	3,47	44,38	51,98	3,48	44,41
90% C+10% D	53,38	2,17	44,22	52,83	2,78	44 30	52,66	2,69	44,29
95% C+ 5% D	54,64	1,08	44,03	54,06	1,82	44,10	53,81	1,82	44,18

TABLE 3

Mixture	Loss of weight in the lst step (%)	Loss of weight in the 2nd step (%)	Total loss of weight (%)	CO_2 per cent, determined gasometrically
100% D	22,50	25,60	48,10	47,59
5% C+95% D	21,25	25,60	46,85	47,28
10% C+90% D	20,48	26,83	47,31	47,32
15% C+95% D	19,25	28,00	47,25	47,31
30% C+70% D	16,00	30,75	46,75	47,12
50% C+50% D	10,00	35,50	45,50	45,65
70% C+30% D	7,48	38,00	45,48	45,14
85% C+15% D	5,00	39,75	44,75	44,41
90% C+10% D	5,00	39,25	44,25	44,29
95% C+ 5% D	3,50	40,50	44,00	44,18
100% C	—	44,50	44,50	43,84

TABLE 4

Mixture	Temperature of the lst endothermic peak (°C)	Temperature of the 2nd endothermic peak (°C)	Temperature xf the inflexion point on the TG curve (°C)
100% D	772	875	790
5% C+95% D	782	890	810
10% C+90% D	780	895	808
15% C+85% D	780	890	805
30% C+70% D	780	903	803
50% C+50% D	780	908	800
70% C+30% D	783	923	795
85% C+15% D	780	921	785
90% C+10% D	780	938	790
95% C+ 5% D	778	930	775
100% C	—	918	—

relations were obtained in the course of thermal investigation of 69 carbonaceous rock samples deriving from a sequence of the South Great Plain.

Similarly to the mixture series in case of the demonstrated samples the peak temperature of the first endothermic effect showed much smaller fluctuation than the second (main) one (between 780 and 800 °C). When investigating the temperature of the main endothermic peak it can be stated that the points indicating the samples are divided into two groups. In the samples belonging to the first group the dependence of the temperature of the endothermal effect on the carbonate quantity is more apparent and in spite of all deviations the peak temperature increases. In the second group the peak temperature increases to less considerable extent. In the samples belonging to the first group the maximal carbonate content is 33 per cent, while in the secodn group the minimal quantity of carbonates is 43 per cent. In the samples of the second group the calcite/dolomite ratio determined by means of X-ray diffractometer varies between 100:0 and 90:10 and it rarely decreased to the value of 80:20. The samples of the first group, however, are predominantly dolomitic or the ratio of the two carbonate minerals is nearly the same.

The grain size, however, causes a change which is opposite to that of the quantity. In the DTA-curve of the samples belonging to the second group such secondary effect was observed on the main endothermal effect which relates to the presence of a carbontae phase of finer grain size than the average. This is the explanation that the increase of the temperature of the endothermic main effect is of more moderate rate than in case of the samples of the first group within which the increase of the carbonates' total quantity is the primary determining factor of growth.

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MANGANESE-BEARING SILICATE MINERALS FROM METAMORPHOSED MANGANESE FORMATIONS OF INDIA. III TIRODITE

SUPRIYA ROY

ABSTRACT

Tirodite, the yellow manganiferous amphibole, described first by DUNN & ROY [1938] from metamorphosed manganese formations at Tirodi, Madhya Pradesh, India, has been studied in detail. Earlier workers related this mineral either to richterite or to cummingtonite. Determination of optical properties, X-ray powder data and interpretation of chemical analyses of the mineral from different localities indicate that the composition of tirodite (MnO 2.84 to 13.83%) varies fairly widely within the complete chemical series between tremolite and richterite. The tirodites were found either in an alkali-rich environment in pegmatites which assimilated part of the manganese formation they cut across, or in manganese silicate rocks themselves that have been subjected to soda-metasomatism.

INTRODUCTION

Tirodite, a manganiferous amphibole, with characteristic straw-yellow body colour, was first named and described from the metamorphosed manganese formations of the Precambrian Sausar Group at Tirodi mine, Balaghat District, Madhya Pradesh, India by DUNN & ROY [1938]. The mineral has, since then, been described from metamorphosed manganese formations from different areas in the States of Madhya Pradesh, Maharashtra, Gujarat and Orissa, India. [BABU & NAYAK, 1961; ROY & MITRA, 1964; ROY, 1966; ROY & PURKAIT, 1968; GHOSE *et al.* 1974].

DUNN & ROY [1938] originally suggested that tirodite approaches richterite in composition. BILGRAMI [1955] and BABU & NAYAK [1961] corroborated the above conclusion. ZWANN & VAN DER PLAS [1958] suggested that tirodite is a transitional member between tremolite and richterite but they also pointed out that X-ray data indicate a composition in the glaucophane-crossite group. SEGELER [1961] and KLEIN [1964] related tirodite to manganoan cummingtonite. TRÖGER [1961] concluded from published analyses of tirodite that it must be classified between kupfferite and Na—Ca amphiboles. ROY & PURKAIT [1968] showed that the composition of tirodite from Gowari Wadhona, Madhya Pradesh, occurring at the contact of manganese silicate rocks (gondite) and pegmatites, can be calculated in terms of cummingtonite, tremolite and glaucophane molecules but if the manganese is considered to be restricted entirely to the X site, the composition clearly approaches that of the richterite-tremolite series. GHOSE *et al.* [1974] very recently showed the presence of magnesio-richterite and magnesio-riebeckite as exsolved phases constituting the tirodite sample (from Tirodi) they studied.

MODE OF OCCURRENCE AND PARAGENESIS

Tirodite is fairly well distributed in regionally metamorphosed manganese silicate rocks (gondite) and in pegmatite veins invading the manganese formation in different parts of the Precambrian manganese ore belts of Madhya Pradesh and Maharashtra (Sausar Group) and Orissa (Gangpur Group). The mineral occurs in gondites of both greenschist and amphibolite facies and has also been found in contact metamorphosed manganese silicate rocks (kodurite) of pyroxene-hornfels facies at Jothvad, Gujarat, India [ROY, 1966]. The mineral assemblages from different areas in which tirodite is present, are shown in Table 1.

TABLE 1

Metamorphic grade	Locality	Host Rock	Mineral Assemblage
Greenschist facies	Dongri Buzurg, Maharashtra	Gondite	Tr-Sp-Mp-Br-Qz
Amphibolite facies	Chikla, Maharashtra	Gondite	Tr-Sp-Rh-Ap-Pl-Br-Qz
do	Tirodi, Madhya Pradesh	Gondite	Tr-Sp-Rh-Pl-Qz
		Gondite	Tr-Sp-Mp-Ap-Br-Qz
		Pegmatite	Tr-Bp-Mc-Qz
do	Ramdongri, Maharashtra	Gondite	Tr-Sp-Rh-Br-Jb-Qz
do	Netra, Madhya Pradesh	Gondite	Tr-Sp-Ap-Br-Qz
		Gondite	Tr-Sp-Bp-Rh-Ap-Qz
		Pegmatite	Tr-Bp-Mp-Mc-Qz
do	Gowari Wadhona, Madhya Pradesh	Pegmatite	Tr-Md-Ct-Br-Qz
		Pegmatite	Tr-Pl-Mc-Ct-Qz
Pyroxene-hornfels facies	Jothvad, Gujarat	Kodurite	Tr-Span-Rh-Bp-Mc-Ap-Qz
		Kodurite	Tr-Span-Bp-Ap-Mc-Mp-Qz

Tr- Tirodite, Sp- Spessartite, Span- Spessartite-andradite, Qz- Quartz, Bp- Brown manganiferous pyroxene, Mp- Manganophyllite, Rh- Rhodonite, Pl- Plagioclase, Mc- Microcline, Br- Braunite, Jb- Jacobsite, Ap- Apatite, Ct- Calcite, Md- Manganoan diopside.

In gondites of different metamorphic grades, tirodite is generally present as fine to coarse needles and blades. It occurs in the interstitital spaces of spessartite and rhodonite and also cuts across rhodonite and replaces brown manganiferous pyroxene (aegirine-augite; ROY, 1971) and manganoan diopside along and across cleavage. The mineral is more widespread in pegmatites at the contact of gondite and manganese orebodies and assumes very large dimensions (upto 10.5 long crystals reported, ROY, 1966). The tirodites, by and large, occur in association with rhodonite and brown manganiferous pyroxene and very rarely, if at all, accompanies blanfordite. The affinity of brown manganiferous pyroxene (manganiferous aegirine-augite) to tirodite has already been pointed out by ROY [1971].

TABLE 2

Chemical Composition and Optical Properties of Tirodite

	1	2	3	4	5	6	7	8	9	10
SiO_2	53.25	53.26	53.26	54.88	53.03	54.88	54.54	54.78	51.84	55.08
Al_2O_3	2.31	2.25	1.25	3.04	1.77	2.37	1.50	3.10	4.08	1.17
TiO_2	0.79	0.78	—	0.05	0.75	1.10	0.75	TR	TR	0.17
Fe_2O_3	1.71	2.60	2.63	3.69	11.25	5.67	8.93	1.90	3.28	3.96
FeO	1.62	1.12	1.06	0.62	TR	TR	TR	1.01	TR	3.17
MgO	28.42	29.16	31.26	20.81	16.84	17.33	17.11	17.02	16.71	17.52
MnO	4.66	6.24	8.25	5.36	2.84	10.14	7.77	13.21	13.43	10.52
CaO	3.42	1.10	1.11	8.28	4.17	3.34	3.11	6.17	8.01	3.32
Na_2O	1.125	1.39	1.56	2.09	5.02	3.14	4.84	0.83	1.14	2.65
K_2O	0.06	0.09	0.07	0.48	1.03	0.42	1.08	0.05	0.24	0.74
H_2O^+	[2.04	[1.87	[0.05	1.13	0.40	0.70	0.38	1.76	1.10	1.32
H_2O^-				0.08	3.25	0.12	0.14	0.16	0.18	0.14
F	—	—	—	—	0.08	0.34	0.07	0.41	0.21	0.11
	99.63	99.86	100.50	100.51	100.42	99.55	100.19	100.40	100.22	99.87
$O \equiv F$	—	—	—	—	0.03	0.14	0.03	0.17	0.09	0.05
TOTAL	99.63	99.86	100.50	100.51	100.39	99.41	100.19	100.23	100.13	99.82
100 Mg:(Mg+ $Fe^{2+}+Fe^{3+}+Mn$)	86.72	84.31	81.53	80.12	69.79	66.67	65.72	65.33	64.25	64.25
					$\Sigma(O, OH, F)=24$					
Si	7.29	7.38	7.56	7.71	7.85	7.95	7.91	7.84	7.57	7.96
Al	0.52	[0.62 [0.04	0.21	[0.29 [0.20	[0.15 [0.16	[0.05 [0.36	[0.09 [0.17	[0.16 [0.36	[0.43 [0.27	[0.04 [0.16
Ti	0.16	0.08	—	0.01	0.08	0.11	0.08	—	—	0.02
Fe^{3+}	0.18	0.27	0.27	0.39	1.25	0.62	0.97	0.21	0.36	0.43
Fe^{2+}	0.18	0.12	0.12	0.07	—	—	—	0.12	—	0.38
Mg	5.88	6.02	6.05	4.39	3.72	3.74	3.70	3.63	3.63	3.78
Mn	0.54	0.73	0.98	0.63	0.36	[0.17 [1.08	[0.08 [0.88	[0.68 [0.92	[0.74 [0.92	[0.23 [1.06
Ca	0.51	0.16	0.15	1.25	0.66	0.52	0.48	0.95	[1.08 [0.18	0.51
Na	0.32	0.37	0.41	[0.12 [0.46	[0.98 [0.46	[0.40 [0.48	[0.64 [0.72	[0.13 [0.10	0.32	[0.43 [0.32
K	0.00	0.01	0.01	0.08	0.19	0.08	0.20	0.01	0.04	0.13
OH	1.86	1.72	0.00	1.13	0.39	0.68	0.37	1.68	1.07	1.27
F	—	—	—	—	0.07	0.15	0.03	0.18	0.10	0.05
ΣZ	7.81	8.00	7.77	8.00	8.00	8.00	8.00	8.00	8.00	8.00
ΣY	6.40	6.53	6.44	5.06	5.21	5.00	5.00	5.00	5.00	5.00
ΣX	1.37	1.27	1.55	2.00	2.00	2.00	2.00	2.00	2.00	2.00
ΣA	0.00	0.00	0.00	0.54	0.65	0.56	0.92	0.11	0.54	0.45
					OPTICAL PROPERTIES					
α	1.629	1.629	1.629*	1.617	1.627*	1.632*	1.628*	1.626*	1.630*	1.631*
β	—	—	1.639*	1.631	—	—	—	—	—	—
γ	1.650	1.650	1.650*	1.637	1.649*	1.652*	1.650*	1.648*	1.651*	1.650*
α	—	—	Colourless to pale yellow	Pale Yellow	Colourless	Very pale Yellow	Colourless	Pale Buff Buff	Pale yellow Yellow	Colourless Pale Yellow
β	—	—	—	Pale Yellow	Pale Yellow	Pale Yellow	Pale Yellow	Yellowish	Yellow with	Pale yellow with
γ	—	—	Pale yellow to straw yellow	Straw yellow	Yellow	Straw Yellow	Pale yellow with greenish tinge	Brown	brownish and greenish tinge	greenish tinge
γ:[001]	18°	17°	21°	—	22°	20°	24°	23°	22°	20°
$2V_x$	41°	37°	88°	68°	80°	78°	66°	82°	80°	78°
Analyst:	S. A. Bilgrami	R. K. Phillips	P. C. Roy	S. K. Babu	P. B. Gupta	B. P. Gupta	B. P. Gupta	B. P. Gupta	B. P. Gupta	B. P. Gupta

* ±0.002

1. Tirodite, Tirodi, Madhya Pradesh [Bilgrami, 1955]
2. Tirodite, Chikla, Maharashtra [Bilgrami, 1955]
3. Tirodite, Tirodi, Madhya Pradesh [Dunn & Roy, 1938]
4. Richterite (Tirodite), Miragpur, Madhya Pradesh [Babu & Nayak, 1961]
5. Tirodite, Sitapatore, Madhya Pradesh [Roy, 1966]
6. Tirodite, Ramdongri, Maharashtra [Present study]
7. Tirodite, Gowari Wadhona, Madhya Pradesh [Roy & Purkait, 1968]
8. Tirodite, Gara, Madhya Pradesh [Present study]
9. Tirodite, Mansar, Maharashtra [Present study]
10. Tirodite, Dongri Buzurg, Maharashtra [Present study].

CHEMICAL COMPOSITION, OPTICAL PROPERTIES AND X-RAY DATA OF TIRODITE

The chemical composition and optical properties of tirodite cocurring in metamorphosed manganese formations in different localities of Madhya Pradesh and Maharashtra (Sausar Group) have been compiled in Table 2. The X-ray powder data of tirodite (Analysis No. 6., Table 2) from Ramdongri, Maharashtra are given in Table 3.

DISCUSSION

Survey of earlier literature shows that the mineral tirodite has been considered to be related to either richterite [DUNN & ROY, 1938; BILGRAMI, 19555, BABU & NAYAK, 1961] or cummingtonite [SEGELER, 1961; KLEIN, 1964]. Intermediate composition between the two ($Kupfferite_{50}$ $Calcium\text{-}edenite_{30}$ $Richterite_{20}$) has also been suggested by TRÖGER [1961]. The manganoan cummingtonites described from different areas so far, are pale greyish to light green in hand specimens and colourless to nonpleochroic pale green in thin section in plane polarized light [JAFFE *et al.* 1961; CHAKRABORTY, 1963; KLEIN, 1964], whereas the tirodites are invariably straw yellow to brownish yellow in hand specimens and distinctly pleochroic in shades of yellow in thin sections. The refractive indices of tirodite (α 1.617—1.632, γ 1.637—1.652; Table 2) are much lower than those of cummingtonites and are well within the range of the richterite-tremolite series, though lower R. I. values for manganoan cummingtonites have been reported. The 100 $Mg/(Mg+Fe^{2+}+Fe^{3+}+Mn)$ values for tirodite are in higher range (86.72 to 64.25) than in cummingtonites (67.7 to 33.8; DEER, HOWIE & ZUSSMAN, 1963, pp. 236—237) and approach those for richterite-tremolite series (99.8 to 66.8; DEER, HOWIE & ZUSSMAN, 1963, pp. 354—355). The Fe_2O_3, CaO and

TABLE 3

X-ray Powder Data for Tirodite from Ramdongri, Maharashtra
Cu/Ni Radiation

d (Å)	I	*d*(Å)	I	*d*(Å)	I
8.44	8B	2.944	5	1.653	5
4.82	1	2.723	10	1.587	4
4.456	3	2.55	6B	1.512	4B
3.84	W	2.302	6B	1.435	5
3.415	7	2.175	6B	1.378	4
3.245	4	2.039	4B	1.344	4
3.112	7	1.88	W8	1.289	5B

Na_2O contents of tirodites, though variable (Fe_2O_3 — 1.91 to 11.25, CaO — 1.10 to 8.28, Na_2O — 0.83 to 5.02; Table 2), in general, approach the range for richterite-tremolite and are much higher for cummingtonite. Also the FeO content of tirodite is negligible compared to the high FeO content of cummingtonite.

For these alkali-rich amphiboles, with a general formula of $AX_2Y_5Z_8O_{22}(O, OH, F, Cl)_2$, the allocation of Mn in either *X* or *Y* site is important. In most cases, there is too much of manganese to be allocated wholely to *Y* site and a part most certainly

occupies the *X* position. The proportion between the amount of Mn in *X* and *Y* sites is variable (PHILLIPS & LAYTON, 1964). In the *X* site, Mn apparently replaces Ca.

In analyses nos. 1, 2, 3, 4, 5 (Table 2) the *Y* site is oversubscribed (>5.00) without considering Mn at all and in analyses 6, 7, 8, 9, 10, Mn is divided between *X* and *Y* sites with the larger part invariably in the *X* site. Thus, in all probability, Mn largely replaces Ca in preference to (Mg, Fe^{2+}) in tirodite.

When the analyses of tirodite in Table 2 were recalculated to the basic formula of amphiboles, with Na representing all cations in *A* site, Ca representing Ca+Mn in *X* site, Mg representing Mg+Mn and Al representing Al+Fe^{3+}+Ti in *Y* site [PHILLIPS & LAYTON, 1964, p. 1107], analyses nos. 1, 2, 3, 4, 8, 9 & 10 indicate a composition approaching that of tremolite with some sodium and analyses nos. 5, 6 & 7 approach richterite composition (varying from Na_2Ca to $NaCa_{1.5}$ atoms per formula unit; SUNDIUS, 1946). It, therefore, indicates that the tirodites correspond to manganoan tremolite-richterite, with the composition varying fairly widely within the complete chemical series between tremolite and richterite.

Very recently GHOSE *et al.* [1974] have shown by electron microprobe analysis, electron microscopy and single crystal X-ray diffraction that tirodite from Tirodi show magnesio-richterite and magnesio-riebeckite as two exsolved phases, indicating a miscibility gap between the two. They stated that the bulk composition of tirodite approaches that of magnesio-richterite (with only small magnesio-riebeckite) on the basis of extremal composition determined in clear patches in tirodite by electron microprobe analysis. None of the analyses of bulk tirodite samples (clean one-phase samples subject to the resolution of polarising microscope) presented in Table 2 approaches the composition of magnesio-richterite ($Na_2Mg_6Si_8O_{22}(OH)_2$) which was known [before GHOSE *et al.* 1974] only as a synthetic phase. However, analyses nos. 5 and 7 approach a composition intermediate between richterite and magnesio-richterite as synthesized by CHRISTOPHE-MICHEL-LEVY [1957].

As already stated, tirodite is found to occur largely in the pegmatite veins at their contact with manganese silicate rocks or manganese orebodies. It is also found in the regionally and contact metamorphosed manganese silicate rocks (gondite and kodurite, respectively) themselves. It is evident that the tirodites were formed in the pegmatites in an alkali-rich environment and the manganese was derived from the host rocks by assimilation. In the gondites and kodurites the tirodites were formed by soda metasomatism during the emplacement of the pegmatites.

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MANGANOAN SPHENE FROM GARRA BALAGHAT DISTRICT, MADHYA PRADESH, INDIA

SUPRIYA ROY

At Garra, Balaghat Districht, Madhya Pradesh, India, regionally metamorphosed manganese orebodies and manganese silicate rocks (gondite) occur as interbanded bodies in Precambrian Sausar Group and these are often cut across by pegmatite veins and dikes of different dimensions. The gondites and manganese orebodies occupy the Lohangi zone at the contact of Mansar and Lohangi Formations of the Sausar Group and are made up of spessartite-quartz-rhodonite and the lower oxides of manganese, respectively. The discordant pegmatite bodies of calcalkaline composition, at their contact with gondite and manganese orebodies, show concentration of manganese-bearing silicate minerals such as blanfordite, winchite, spessartite, tirodite and brown manganiferous pyroxene. The manganoan sphene belongs to the assemblage blanfordite-winchite-quartz-sodic plagioclase-microcline-apatite, developed by the interaction of the pegmatite fluid with the manganiferous country rock.

OPTICAL PROPERTIES

The sphenes are developed as well formed wine-red crystals that show, under the microscope, the following scheme of pleochroism:

α = pale yellow with a greenish tinge
β = pale pink with greenish tinge
γ = salmon pink.

The refractive indices of the mineral are very high. $\alpha = 1.847 \pm .006$. γ could not be measured (due to nonavailability of liquids with $n > 1.90$) though it is much higher than 1.90. The birefringence, as apparent from interference colour, is also very high. $2\dot{V}_\gamma = 38°$; $\gamma:[001] = 45°$.

CHEMICAL COMPOSITION

A separated and cleaned sample of sphene was chemically analysed and the results are given in Table 1. The X-ray powder data of the mineral has been given in Table 2.

The manganese content of this sphene is unusually high and it apparently replaces Ca in the structure. The TiO_2 content is slightly low and the Al_2O_3 and Fe_2O_3 content high and these, together with the high value of optic axial angle and relatively

TABLE 1

Chemical composition of manganoan sphene

	wt%	No. of ions on the basis of 24(O, OH, F)	
SiO_2	29.94	3.87	
		[0.13]	4.00
Al_2O_3	9.20	[1.26]	
TiO_2	30.20	2.95	
Fe_2O_3	3.16	0.31	4.63
FeO	0.56	0.06	
MgO	0.30	0.05	
MnO	1.82	0.20	
CaO	23.97	3.33	3.63
Na_2O	0.23	0.05	
K_2O	0.35	0.05	
H_2O^+	0.42		0.38 OH
H_2O-	0.14		
TOTAL	100.29		

ANALYST— B. P. GUPTA

TABLE 2

X-ray powder data of manganoan sphene, Cu/Ni radiation

d(Å)	I	*d*(Å)	I	*d*(Å)	I	*d*(Å)	I
4.93	5	2.364	w	1.806	2	1.503	4
3.247	10	2.277	5	1.729	5VB	1.421	4B
3.00	8	2.113	1	1.645	5	1.35	3
2.831	VW	2.071	5	1.561	3	1.308	3
2.611	10	1.953	1	1.531	2	1.28	1

low R. I. (within the range for sphene), indicate that the mineral corresponds to the manganoan grothite variety [DEER, HOWIE and ZUSSMAN, 1963, p. 71].

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MINERALOGY AND CHEMISTRY OF A PEGMATITIC FELDSPAR FROM HAFAFIT, EGYPT

A. A. EL SOKKARY

ABSTRACT

This pegmatitic feldspar is a perthite composed of microcline and low albite roughly in the ratio of 2:1. The microcline is of high triclinicity (0.84). Chemically this alkali feldspar contains 10.58% K_2O, 3.37% Na_2O and 0.25% CaO. These are equivalent to 62,6% microcline, 28,5% albite and 1.2% anorthite. The plagioclase intergrown with microcline is albite with 4% An. The feldspar in question shows enrichment in Rb and Y with depletion in Sr, Ba and Zr, these characterize strongly fractionated rocks. The enclosing pegmatite is shown to be most probably one of the latest residues of a fractionally crystallizing magma directly formed at low temperature range.

The present pegmatite is to be contrasted, on mineralogical and geochemical grounds, with the garnetiferous pegmatite of W. Gemal area. Thus two distinctive types of pegmatites are recognized in the south Eastern Desert of Egypt.

INTRODUCTION

Acid pegmatites, generally of granitic composition, occur at the Hafafit area, south Eastern Desert of Egypt. Some of these pegmatites show abnormal coarse development of their alkali feldspars. It was thought that detailed mineralogical and chemical study of these feldspars might be useful and serve as multipurpose. In the first place it may help in solving problems related to the genesis of the enclosing pegmatite. Secondly feldspars start to have wide applications in the fields of waste disposal of nuclear materials as well as in ion exchange studies. Before testing such possibilities, a mineralogical and chemical study of the feldspars in question is prerequisite. Thirdly to examine the possiblity of using these feldspars as natural silicate standards.

MINERALOGY

The pegmatitic rock is very coarse grained, composed exclusively of big feldspar crystals sometimes with intergrown quartz. It is white in color with specific gravity 2.57. The rock shows signs of being subjected to pressure. The feldspar is potash feldspar because it is stained yellow with sodium cobaltinitrite test.

Under the microscope, the rock is composed of microcline, albite and quartz. The microcline develops two prominent sets of cleavage, but so far no crosshatched twinning is observed. This microcline is intergrown with plagioclase strings giving rise to perthitic texture. The latter texture is as well visible in hand specimen. There are small quartz inclusions showing undulatory extinction and assuring that the rock was subjected to strain.

The material is ground to pass 150 mesh, the powder is then subjected to diffrac-

TABLE 1

Partial diffraction pattern of the analysed feldspar

d (Å)	I/I.	Mineral	d (Å)	I/I.	Mineral
6.57	9	Ab	2.90	6	M
6.41	7	Ab	2.76	2	M
4.23	8	M+Qz	2.62	2	M+Ab
4.04	4	M+Ab	2.57	4	Ab
3.98	4	M	2.53	2	M
3.85	5	M	2.43	2	M+Ab
3.80	5	Ab	2.34	2	M+Ab
3.72	4	?	2.16	9	M+Ab
3.68	5	M+Ab	2.13	1	M+Ab
3.60	2	M	1.99	1	M+Ab
3.50	9	M	1.93	1	M+Ab
3.38	8	M	1.86	2	M+Ab
3.30	10	Qz	1.81	7	M+Ab+Qz
3.27	100	M	1.62	1	M
3.22	47	Ab	1.57	2	Ab
3.03	3	M	1.51	1	M+Ab
2.96	6	M+Ab	1.46	2	M+Ab

tion analysis. The instrument used is a Philips chart recorder diffractometer (type PW—1010) with the following instrumental settings: radiation Cu (K_α) with wavelength 1.5418 Å, filter Ni, current 20 mA, tension 36 KV, range of 2Θ: 5—65°, scale 4. Table 1 gives partial diffraction pattern of the analyzed alkali feldspar. The following symbols are used to designate the corresponding minerals: M: microcline, Ab: albite and Qz: quartz.

The diffraction pattern shows clearly that the analyzed alkali feldspar is microcline mixed with certain amount of low albite in order to form perthite. The ratio of microcline to albite is roughly 2:1. There are minor amounts of quartz appearing most probably as inclusions. The triclinicity of this microcline is measured on $131/1\bar{3}1$ faces and found to be 0.84 indicating that it is of high triclinicity *i. e.* high ordering of Si and Al atoms.

MAJOR CONSTITUENTS

Table 2 gives the chemical analysis of the analyzed feldspar rock expressed in weight per cent of the oxides. Analytical techniques are described elsewhere [EL SOKKARY, 1970]. It will be noticed that K_2O content (10.58%) is the highest among the other alkali and alkaline earth elements which give for Na_2O 3.37% and for CaO 0.25%. This assures that the investigated felspar is mainly potassic. Sodium on the other hand is present to a much lesser extent than K and contributes in making the plagioclase intergrown with the potash feldspar. The small amount of CaO appearing in the analysis comes from the plagioclase. If both the quantities of Na_2O and CaO are recalculated as albite and anorthite molecules respectively, it is seen that An/(Ab+An) = 4% roughly, assuring that the plagioclase feldspar intergrown with the potash feldspar is albite.

The K, Na and Ca contents of the analyzed feldspar are converted into the corresponding weigh contents of microcline, albite and anorthite, these are found to be: 62.6%, 28.5% and 1.2% respectively. The quantity of SiO_2 calculated on the

TABLE 2

Chemical analysis of major and minor elements in the analyzed feldspar

Oxide	Weight %
SiO_2	65.90
Al_2O_3	18.97
Fe_2O_3 (total iron)	0.10
MnO	0.01
CaO	0.25
Na_2O	3.37
K_2O	10.58
TiO_2	0.02
P_2O_5	0.01
H_2O^-	0.05
	99.26

basis of the standardized formulae of these three minerals and their percentage composition in the analyzed feldspar is found to be 61.23% as compared with 65.09% given by the chemical analysis. The difference which is equal to 4.67% is attributed to free silica present most probably as inclusions in the feldspar or may be in association with it.

It seems that the amount of total iron (Fe_2O_3=0.10%) is too small to affect the original white color of the feldspar. Quite minor amounts of MnO, TiO_2 and P_2O_5 appear as well in the analysis.

TRACE ELEMENTS

Table 3 gives some trace elements data expressed in ppm in the analyzed feldspar as compared with corresponding values of: (1) K-feldspars separated from strongly fractionated granites from Gebel El Dibai in the Eastern Desert and from Wadi Sidri in Sinai [EL SOKKARY, 1970] (2) Garnetiferous pegmatite from Wadi Gemal

TABLE 3

Some trace elements (ppm) of the analyzed feldspar as compared with those of: (1) Feldspars derived form strongly fractionated granites (2) Garnetiferous pegmatite

Element	Analyzed feldspar	Sibai feldspar	Sidri feldspar	Garnetiferous pegmatite
Ba	Tr*	—	—	—
Rb	420	200	466	31
Sr	<5	14	36	315
Y	21	19	29	502
Zr	32	25	25	168

* Tr = Trace.

area in the south Eastern Desert [KHALIL and EL SOKKARY, 1971]. Trace elements are analyzed by a modified X-ray fluorescence technique [DAMON, 1966].

It is clear from Table 3 that the content of trace elements in the analyzed feldspar and the two feldspars separated from strongly fractionated granites shows general parallelism. The chief characteristic in the three feldspars is an enrichment in Rb together with an impoverishment in Sr. However, Sr in the analyzed feldspar still shows more lowering quantities. Moreover, Y is relatively enriched in these feldspars while Zr tends to be depleted. Barium (Ba) in the analyzed feldspar shows quite dropping quantities.

Thus the analyzed feldspar shows enrichment in Rb and Y together with depletion in Sr, Ba and Zr. These characterize strongly differentiated rocks. Therefore the white pegmatitic feldspar rock from Hafafit is a strongly differentiated acid pegmatite. This is to be contrasted with the garnetiferous pegmatite from W. Gemal area which shows a quite different pattern of distribution of its trace elements as is evident from Table 3. The latter pegmatite is indexed by dropping values of Rb with enrichment trends in Sr, Y and Zr.

It is plausible to say that these two pegmatites, that is to say, the white pegmatitic feldspar rock from Hafafit and the garnetiferous pegmatite from W. Gemal area are the products of two different processes with different times of emplacement.

DISCUSSION

The alkali feldspar under investigation is shown to be a perthite. This perthite is composed of microcline with high triclinicity and low albite in the ratio of 2:1. Quantitative determination of major constituents of this feldspar revealed that $K_2O = 10.58\%$, $Na_2O = 3.37\%$ and $CaO = 0.25\%$. Thus K_2O is the main constituent among alkali and alkaline earth elements. This assures on chemical grounds that the feldspar is mainly potassic, while the intergrown plagioclase is albite with 4% An. Total iron (as $Fe_2O_3 = 0.10\%$) is present in minor amounts, that is why the feldspar keeps a white coloration. From trace elements point of view, the microcline perthite under investigation shows enrichment in Rb and Y together with depletion in Sr, Ba and Zr. This distribution pattern indicates that the pegmatite enclosing the mentioned microcline perthite is a strongly fractionated rock.

It is already argued [EL SOKKARY, 1970] that K-feldspars with low triclinicity characterize metasomatic rocks or rocks undergoing chemical change or local redistribution to form porphyroblasts. Since the K-feldspar under investigation is revealed to be microcline, in the form of perthite, with high triclinicity (0.84), therefore metasomatic processes and any chemical changes are excluded from its formation. Most probably the pegmatite containing the microcline perthite is formed as one of the latest residues of a fractionally crystallizing magma. The distribution of trace elements in this pegmatite as previously outlined adds an additional evidence to this conclusion.

HEIER [1957] could correlate the triclinicity of potash feldspars with their temperature of formation. On the basis of his study, the present microcline perthite with high triclinicity (0.84) has a lower temperature range of formation (400—500 °C). Moreover, the complete absence of crosshatched twinning from this microcline as mentioned in the section on mineralogy may be taken to indicate its direct formation at low temperatures.

In conclusion the microcline pegmatite is most probably one of the latest residues of a fractionally crystallizing magma directly formed at low temperature range. On

the other hand the garnetiferous pegmatite of W. Gemal area is shown to be formed through metamorphic processes [KHALIL and EL SOKKARY, 1971]. Thus two distinctive types of pegmatites are recognized in the south Eastern Desert of Egypt.

An example is choses here to evaluate the applied side of this investigation. TCHELISHCHEV and BORUTZKAYA [1972] were able to show that the maximum exchange capacity sharply increases with the decrease of the X-ray triclinicity from the maximum microcline to orthoclase. Since the present microcline shows maximum triclinicity of 0.84, therefore it is not quite suitable for ion exchange purposes.

The microcline pegmatite contains some quartz in association with the feldspar. This quartz is not homogeneously distributed, a matter which may introduce difficulties in preparing the pegmatite as a local standard silicate rock.

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THE PROBLEMS OF THE PANNONIAN OF HUNGARY

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The Pannonian basin has formed in post-Badenian times in the considerably contracted, gradually bracked and segmented western part of the Paratethys; between the Vienna, Styrian, Croatian and Transsylvanian basins. The extension, the degree of interrelation, the sediment thickness and development of these basins, as well as the fauna, the direction, date and interruption of the faunal migrations necessarily were subordinated to the emergent or submergent movements of the basinal floors and the surrounding mountain chains. These movements resulted in the *occasional* relationships between the Pannonian basin and the Euxinic basin through the Porta Ferrea and the Dacian basin *(Fig. 1)*.

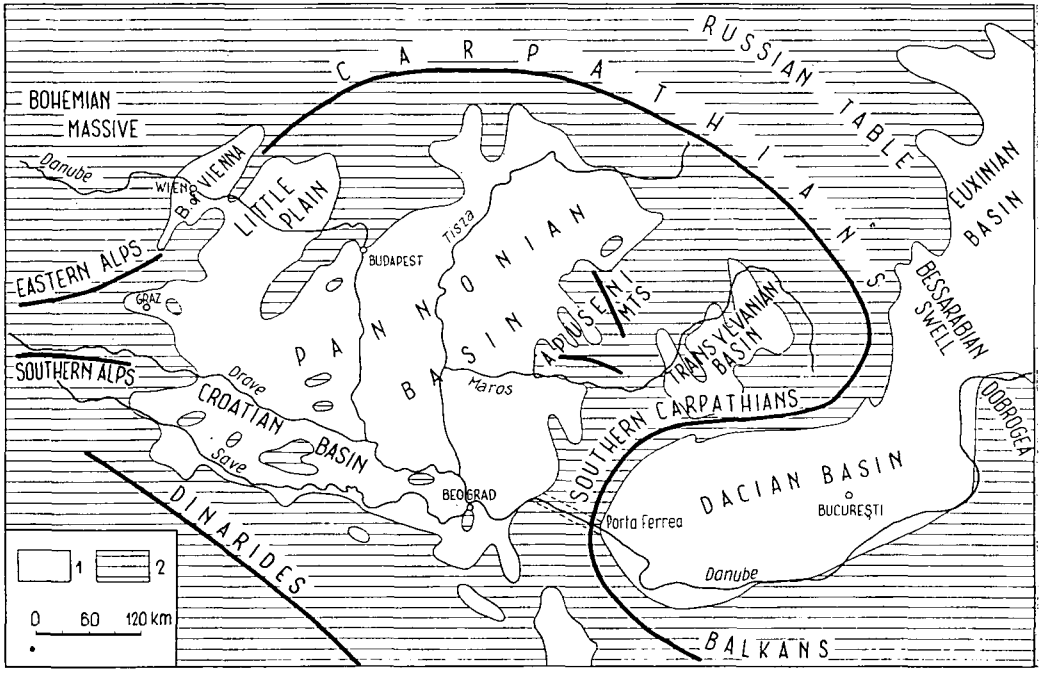

Fig. 1. Location of the Pannonian Basin among the partial basins of the Pliocene Paratethys. *1.* Sea. *2.* Land.

The sediment-mass of the Pannonian exceeds that of any other geological age in Hungary. Its greatest thicknesses are 3500 to 4500 m, and its distribution is country-wide. Surfacial exposures can be found abundatly in its lower and upper parts; the facial and faunal profusion is especially striking in the upper part.

The Pannonian sequences bear a great economic importance: i. e. these accumulate hydrocarbons and water, and contains thick, sub-superficial lignite deposits in several places. Consequently, the deepboring exploration of the Pannonian is statisfying *(Fig. 2)*.

The name Pannonian Stage is used here — in agreement with L. ROTH v. TELEGD [1879] — for the *Congeria*-bearing sequence between the Sarmatian and Pleistocene of the Carpathian basin, as a synonym of the Pliocene. However, the views of the Hungarian and foreign researchers are differently varied about the subdivisioning and parallelization of the certain subdivisions of the Pannonian *(Fig. 3)*.

The first to publish Pannonian fossils was Hörnes, M. (1853—67), from the Vienna basin. The earliest, relatively well determined Pannonian faunas from Hungary and Banat (Kup, Tihany, Radmanest) were described by FUCHS [1870*a*, *b*], but the stratigraphic evaluation was given by Böckh [1874, 1881]. In the years after the turn of the century HALAVÁTS [1911], LŐRENTHEY [1911], VITÁLIS [1911] and LÓCZY, SEN. [1916] raised the number of the known localities over a hundred, and in their faunal lists, numbering some hundred species, many new forms also appeared. These pioneers attempted firstly the parallelization of the Pannonian with the coeval rocks of the surrounding countries. The excessive increase in the number of species raised, even in that time the question of justness of their species concept. However, the first statistical mass-analyses which were suitable for more precise deliminations of the variability ranges were carried out only from the early forties [STRAUSZ 1941*a*, 1942*c*; BARTHA 1954, 1955, 1956, 1959*a*, *b*, 1962, 1963, 1966, 1971*a*].

It was appeared about the Pannonian of Hungary, in the light of the data of boreholes having been increased from the thirties, that

a) in contradiction to the previously presumed 300 m, the maximal thickness is several thousand metres;

b) the cross-section of the sedimentary basin was considerably asymmetrical, and the deepest parts of its floor were situated in the Little Plain and in the southern and south-eastern part of Hungary, i. e. in the marginal parts of the basin [SÜMEGHY 1939, SZÁDECZKY-KARDOSS 1939, SCHRÉTER 1940, DANK 1965, KŐRÖSSY 1968, STRAUSZ 1941, 1942, SZÉLES 1968, 1971*a*, URBANCSEK 1963, VÖLGYI 1965].

The intermittent coring in the hydrocarbon drillings, and the almost entire giving up of the core drilling in the water exploration encumbers markedly the detailed mass-investigations, just as that mistaken view, wich have attempted to overcome the problems arised from the continuously increasing data by the unjustified oversimplification of the geological events. On the other hand, the present writer showed through several examples that the sedimentological and faunal studies by every 10 cm leads to the following advantages:

a) Besides the statistically based separation of species having appeared abundantly in specimens, these studies enable to trace the horizontal (i. e. within beds) and the vertical (i. e. through beds) variability of the forms, that is to recognize racial disintegrations in space, and speciations in time together.

b) These studies supply realistic ground for the layer by layer comparison of the bio-associations, for the interpretation of the temporal and spatial variations in the faunal spectrum and the biofacies, together with the quantitative evaluation, on the basis of the principle: "from more the more, from few a few remains".

c) These studies make the manifold and detailed correlation of the faunas and sediments possible.

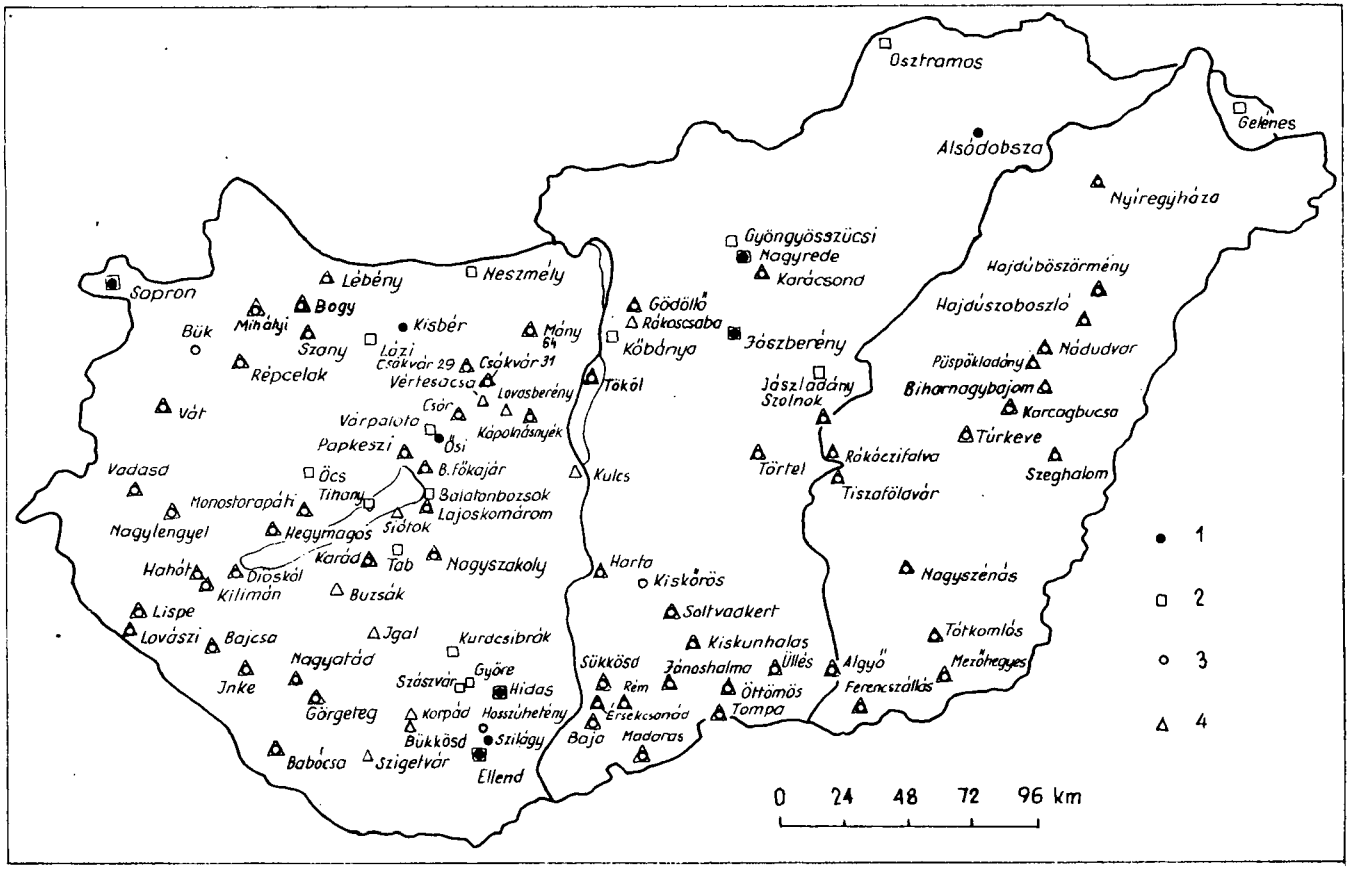

Fig. 2. The most important outcrops of the Pannonian sequence in Hungary.

1. Early Pannonian standard profiles. *3.* Late Pannonian standard profiles. *3.* Boring with Early Pannonian sequence.*4.* Boring with Late Pannonian sequence.

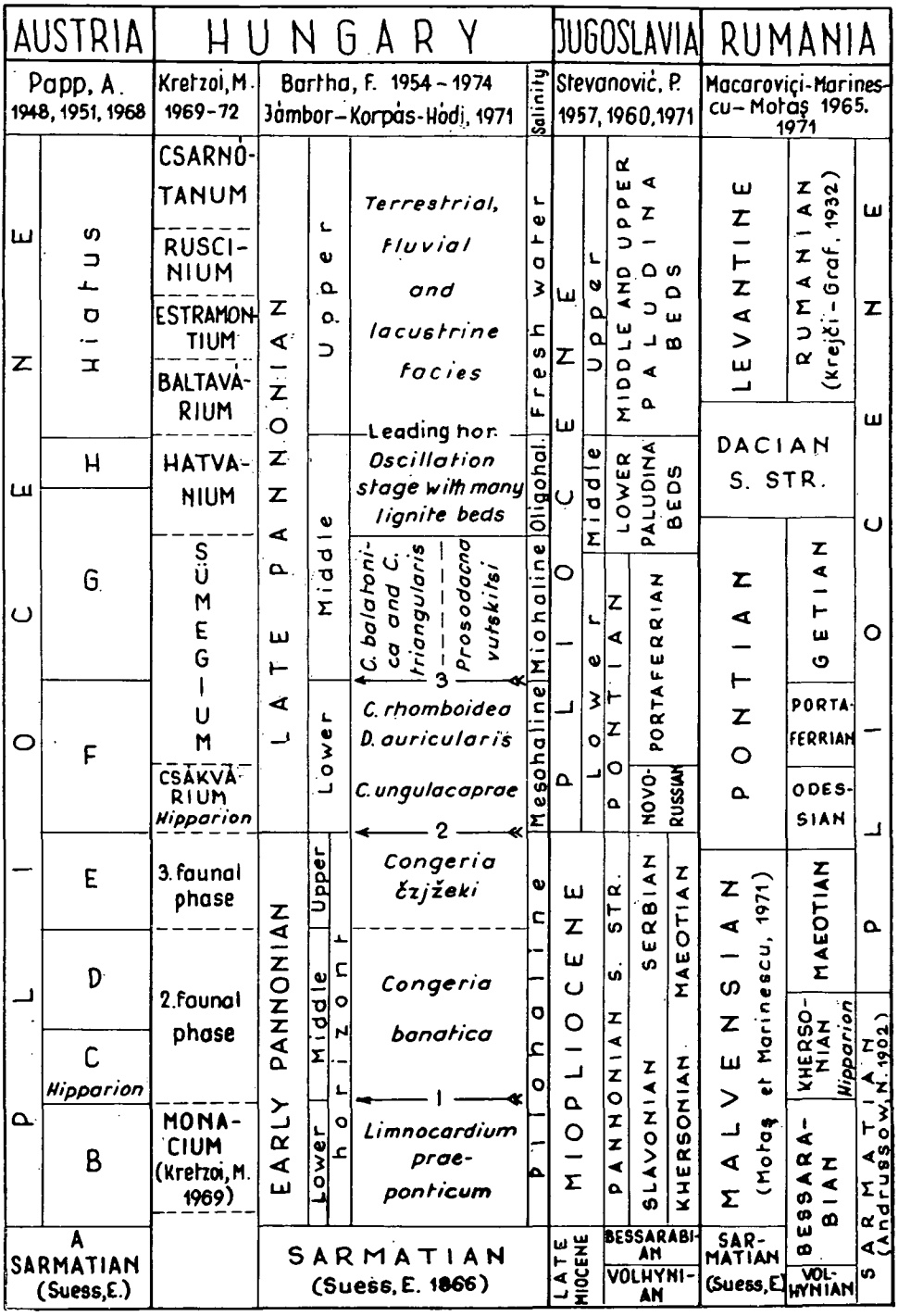
AUSTRIA
HUNGARY
JUGOSLAVIA
RUMANIA
Papp, A. 1948, 1951, 1968
Kretzoi, M. 1969-72
Bartha, F. 1954-1974
Jámbor-Korpás-Hódi, 1971
Salinity
Stevanović, P. 1957, 1960, 1971
Macarovici-Marinescu-Motaș 1965. 1971
NEOGENE
PLIOCENE
Hiatus
H
G
F
E
D
C
Hipparion
B
A SARMATIAN (Suess, E.)
CSARNOTANUM
RUSCINIUM
ESTRAMONTIUM
BALTAVARIUM
HATVANIUM
SMEGMUM
CSÁKVÁRIUM
Hipparion
MONACIUM (Kretzoi, M. 1969)
3. faunal phase
2. faunal phase
EARLY PANNONIAN
LATE PANNONIAN
Upper
Middle
Lower
Lower horizont
Terrestrial, fluvial and lacustrine facies
Leading hor.
Oscillation stage with many lignite beds
C. balatonica and C. triangularis
Prosodacna vutskitsi
3
C. rhomboidea
D. auriculatis
C. ungulacaprae
2
Congeria čzjžeki
Congeria banatica
1
Limnocardium praeponticum
Fresh water
Oligohal.
Mohaline
Mesohaline
Pliohaline
SARMATIAN (Suess, E. 1866)
MIOPLIOCENE
LATE MIOCENE
PANNONIAN S. STR.
SLAVONIAN
SERBIAN
KHERSONIAN
MAEOTIAN
BESSARABIAN
VOLHYNIAN
PLIOCENE
Lower
Middle
Upper
PONTIAN
NOVO-RUSSIAN
PORTAFERRIAN
PALUDINA BEDS
LOWER
MIDDLE AND UPPER
PALUDINA BEDS
MALVENSIAN (Motaș et Marinescu, 1971)
SARMATIAN (Suess, E.)
BESSARABIAN
VOLHYNIAN
KHERSONIAN
Hipparion
MAEOTIAN
PONTIAN
ODESSIAN
PORTAFERRIAN
GETIAN
DACIAN S. STR.
LEVANTINE
RUMANIAN (Krejči-Graf, 1932)
SARMATIAN (Andrussow, N. 1902)
PLIOCENE

Fig. 3

In the course of their revisions on the profile of Fehérpart, Tihany, the present writer [BARTHA 1959*a,b*] and ZALÁNYI [1959*a*] proved that the complexity of the studies can considerably enlarge when taking the mollusc and ostracodes together into consideration, and when comparing the biofacies curve to the grain-size distributional curves. Taking all these, just as the conclusions of PAPP [1951] about the salinity of the Pannonian Lake, into account the parallel running of the two curves could have been unequivocally due to the result of oscillation. On the other hand, the faunal enrichment of the Upper Pannonian as compared to that of the Lower Pannonian could have been interpreted by the hypothesis suggested by STEVANOVIĆ [1951, 1955, 1959, 1960, 1971, STEVANOVIĆ and MLADENOVIĆ 1956], namely that in latest Early Pannonian times the Pannonian basin was temporarily connected to the Dacian basin, through the *Porta Ferrea* canal. This gateway made the migration of such species possible, which would be hardly generated from the Lower Pannonian forms, even with the supposition of pleiotropic mutations.

In the following the paleogeographical reconstructions of the Pannonian horizons are given upwards, referring at the same time to the differences of these horizons, too.

THE PROBLEM OF THE SARMATIAN-PANNONIAN BOUNDARY

At the boundary between the Vienna basin's Sarmatian and Pannonian HOERNESS, R. [1900] and FUCHS and KARRER [1870] postulated a break. On the other hand FUCHS [1870*a,b*], HALAVÁTS [1911] and LÓCZY, SEN., suggested continuous sedimentation within the Pannonian basin. On the basis of the litho- and chronofacies GAÁL [1912, 1938] rendered again a hiatus probably.

At the base of the Pannonian, continuous sedimentation, as well as uncomformity are equally possible; but the areal distribution and degree of the latter is not cleared up so far. The Sarmatian species in the "intermediate" fauna of the Virágvölgy-valley of Sopron [VITÁLIS 1951] are presumably redoposited. According to BÖCKH [1881], FERENCZI [1937] and VADÁSZ [1935], the Sarmatian ended with regression along the coastal lines (e. g. in the Mecsek Mountains). South of the Mecsek Mountains, in the continuous sections of boreholes *Hidas—53* and *Ellend—1* some traces of shallowing (i. e. occurrence of *Orygoceras* sp., *Planorbis* sp., carbonized plant remains) were recognized at the Sarmatian-Pannonian boundary [BARTHA 1966]. However, according to KŐRÖSSY [1968], the sedimentation could have been continuous only is smaller relict lakes, because in latest Sarmatian times the major part of the Pannonian basin emerged by the Attic synorogenic movements, and became the region of the „pre-Pontian erosion". SZÉLES [1971*a*] similarly inferred continuous sedimentation enduring from the Sarmatian to the Pannonian only within the deepest basinal parts, just as the Békés depression. ZALÁNYI [1955, 1956, 1959*b*] frequently found, even in the central part of the Pannonian basin (Great Plain), sapropelic swamp deposits between the Sarmatian and the *Amplocypris-*, *Heterocypris*-bearing strata

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Fig. 3. Presumable correlation of the Pliocene chronotaxons established for the different partial basins. *Based mainly on the authors named in the table, with regard to the publications of* EBERSIN, A. G. ET AL. [1966, KOJUMDGIEWA, E. [1971], MACAROVICI, N. ET AL. [1966], MARINESCU, F. [1973], MOTAŞ, I.—MARINESCU, F. [1971], PANĂ, J. [1971] and POPOV, N. [1971], too. However, it must be noted that both the names and extentes of the individual unities applied by the Rumanian geologists are nowadays subjected to a nearly perpetual change. For example, after MOTAŞ, I. ET AL. [1973], the Pontian can be divided into Portaferrian and Bosphorian, the Dacian, however, into Getian and Parscovian. It is clear that the sense of all these terms fairly differs from the one in the *Fig. 3.*

The arrows with numbers indicate the time of the temporary communications between the Pannonian and Dacian basin through the Iron Gate *(Porta Ferrea)*. In our opinion this communication took place three times during the Pliocene.

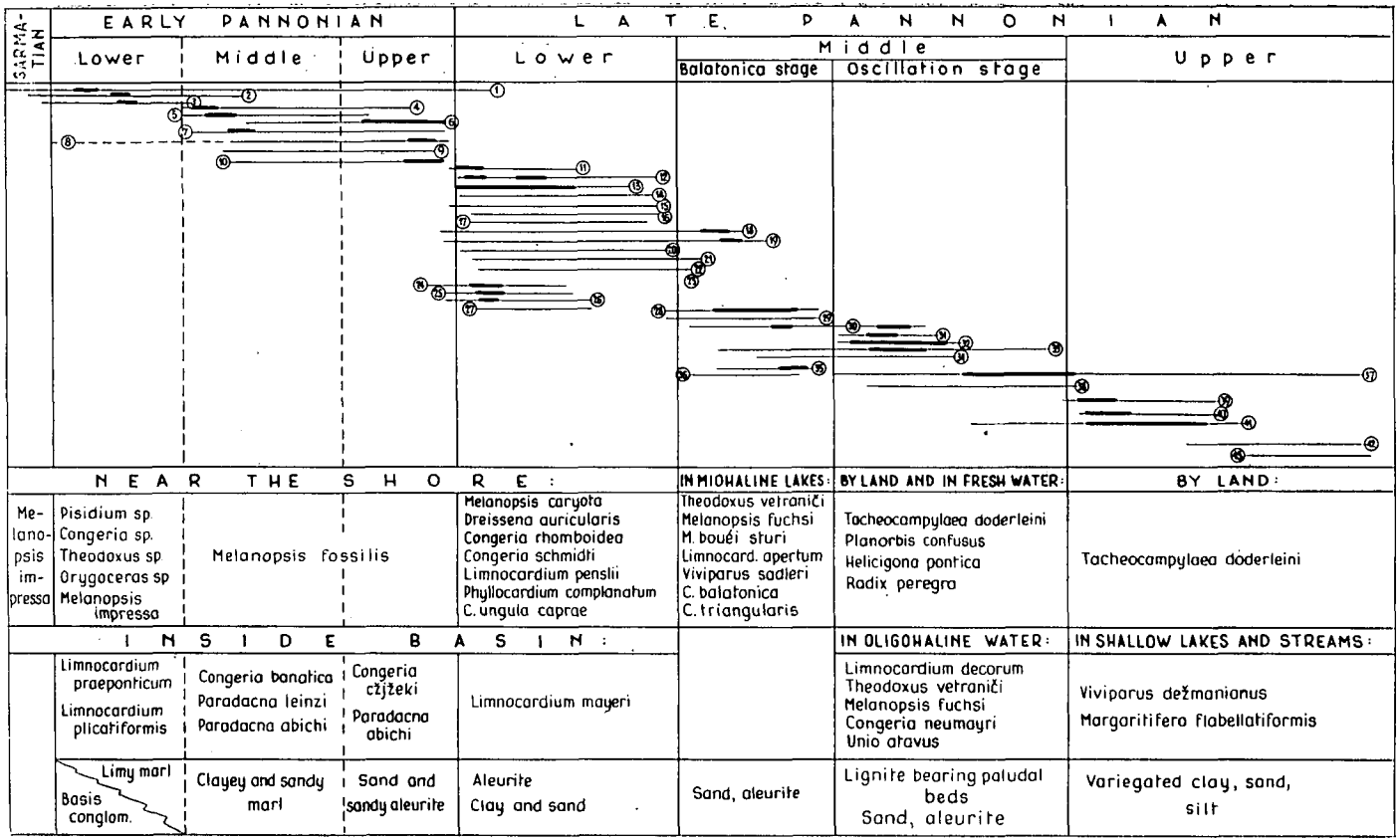
SARMATIAN
EARLY PANNONIAN
Lower
Middle
Upper
LATE PANNONIAN
Lower
Middle
Balatonica stage
Oscillation stage
Upper
NEAR THE SHORE:
IN MIOHALINE LAKES:
BY LAND AND IN FRESH WATER:
BY LAND:
Melanopsis impressa
Pisidium sp.
Congeria sp.
Theodoxus sp.
Orygoceras sp.
Melanopsis impressa
Melanopsis fossilis
Melanopsis carvota
Dreissena auricularis
Congeria rhomboidea
Congeria schmidti
Limnocardium penslii
Phyllocardium complanatum
C. ungula caprae
Theodoxus vetranici
Melanopsis fuchsi
M. bouéi sturi
Limnocard. apertum
Viviparus sadleri
C. balatonica
C. triangularis
Tacheocampylaea doderleini
Planorbis confusus
Helicigona pontica
Radix peregra
Tacheocampylaea doderleini
INSIDE BASIN:
IN OLIGOHALINE WATER:
IN SHALLOW LAKES AND STREAMS:
Limnocardium praeponticum
Limnocardium plicatiformis
Congeria banatica
Paradacna leinzi
Paradacna abichi
Congeria czjzeki
Paradacna abichi
Limnocardium mayeri
Limnocardium decorum
Theodoxus vetranici
Melanopsis fuchsi
Congeria neumayri
Unio atavus
Viviparus dežmanianus
Margaritifera flabellatiformis
Limy marl
Basis conglom.
Clayey and sandy marl
Sand and sandy aleurite
Aleurite
Clay and sand
Sand, aleurite
Lignite bearing paludal beds
Sand, aleurite
Variegated clay, sand, silt

Fig. 4

of the Lower Pannonian *Congeria balatonica* Horizon. On the other hand, the "white calcareous marl" of the basinal parts of the Great Plain and Southern Transdanubia, which is alternately renged into the Sarmatian of into the Lower Pannonian by different authors, presumably shows continuous deposition between the two stages. JÁMBOR and KORPÁS-HÓDI [1971], on the basis of complex studies of the samples from 123 coring drillings, postulated a break of sedimentation only in the case, when the Lower Pannonian rests on Badenian or older rocks, with the complete absence of the Sarmatian. According to them:

a) Continuous transition can be concluded in the case of offshore sedimentation, i. e. when both the Sarmatian and Lower Pannonian are represented at the boundary by argillaceous marls, which can be separated merely by their different mollusc faunas. On the other hand, the continuity is signified also by the mutational steps of the faunas in the boundary strata.

b) Continuous sedimentation can be concluded when Lower Pannonian strata suggesting deepening (e. g. pearl-gravel, argillaceous marl) rest comformably on the shallow-water Sarmatian coarse limestone. The conclusion can be similar when the stronger agitation of the transgressive water-mass, by means of the removal of the sediments, gives the impression of erosional unconformity. In these cases (on this part of Transdanubia) the degree of the subaqueous erosion can be measured by the help of the dacite-tuff index-layers interbedded to lower part of the Lower Pannonian.

c) Continuous deposition can be, at last, concluded, when the Sarmatian-Lower Pannonian boundary runs within sequences consisting in dense alternation of layers of varied — e. g. draining-lagoonal, brackish, swampy and marine — facies, or within series of terrestrial deposits. To draw the boundary can be maked easier by the disappearance of the *Foraminifera* and the genus *Cardium*, as well as by the appearance of the larger *Ostracoda* and the genus *Limnocardium* in the first case, and by observing the start of a new cycle in the second one.

Despite of the water-freshening which continued from the Badenian onwards, and the observed traces of the Late Sarmatian regression, the Sarmatian (and Lower Pannonian) overlaps the earlier Badenian (and, respectively, Sarmatian) rocks in several Hungarian localities. This phenomenon is mainly the result of that the previous, relatively steady submergence slowed down from the Late Badenian, and the neighbouring floor-blocks moved often in the opposite direction. This fact — together with the process of the filling-in — resulted in the temporary stopping of the water-covering in some places, and in the continuance of that in other ones.

The *boundary problem* of the Sarmatian and Pannonian is independent naturally of the fact that the Sarmatian of Hungary can be correlated to only two *(Volhynian+ +Lower Bessarabian)* of the three stages established by ANDRUSOW [1902] for the Russian Sarmatian [SCHRÉTER 1912, 1941, VITÁLIS 1951, BODA 1959, 1971, JÁMBOR 1971*a*]. Consequently, in the case of continuous deposition, the lower part of the Lower Pannonian corresponds in time to the Kherzonian of the Euxinic basin. This latter, however, can be ranged into the Pliocene all the more, because its fauna differs from that of the lower two ages of the Russian Sarmatian at least as much as from the fauna of the paleogeographically separated Early Pannonian.

Fig. 4. Abundances chronological spans and assemblages of the most important molluscan species in the Pliocene of Hungary.

1. *Melanopsis impressa* KRAUSS. 2. *Orygoceras dentaliforme* BRUSINA. 3. *Limnocardium praeponticum* KRAMB. 4. *Congeria banatica* R. HOERN. 5. *Paradacna lenzi* (R. HOERN.) 6. *Congeria czjžki* M. HÖRN. 7. *Paradacna abichi* R. HOERN.). 8. *Melanopsis fossilis* MART. ET GMEL. 9. *Congeria partschi* CŽJŽ. 10. *C. subglobosa* R. HOERNES. 11. *C. ungulacaprae* MÜNST. 12. *C. rhomboidea* M. HÖRN. 13. *Dreissena auricularis* FUCHS. 14. *Limnocardium penslii* FUCHS. 15. *L. majeri* M. HÖRN. 16. *Phyllocardium complanatum* (FUCHS). 17. *L. rothi* HAL. 18. *L. apertum* MÜNST. 19. *Micromelania laevis* FUCHS. 20. *Dreissensiomya intermedia* FUCHS. 21. *Melanopsis pygmaea* PARTSCH. 22. *Gyraulus tenuis* (FUCHS). 23. *G. inornatus* (FUCHS). 24. *Limnocardium schmidti* M. HÖRN. 25. *Congeria zagrabiensis* BRUS. 26. *Kaladacna steindachneri* (BRUS.). 27. *Valvata variabilis* FUCHS. 28. *Congeria triangularis* PARTSCH. 29. *C. balatonica* PARTSCH. 30. *Limnocardium decorum* FUCHS. 31. *Congeria neumayri* ANDR. 32. *Viviparus sadleri* PARTSCH. 33. *Melanopsis fuchsi* (HANDM.). 34. *Theodoxus vetranići* (BRUS.). 35. *Unio atavus* PARTSCH. 36. *Planorbis confusus* SOÓS. 37. *Tachaeocampylaea doderleini* BRUS. 38. *Helicigona pontica* HAL. 39. *Viviparus stricturatus* NEUM. 40. *V. mažuranići* BRUS. 41. *Margaritifera flabellatiformis* (GRIG.—BREZ.). 42. *Dreisenna polymorpha* PALLAS. 43. *Viviparus dežmanianus* BRUS.

Some geochemical differences between the Sarmatian and Pannonian sediments also appear, namely the $CaCO_3$-content averages 70—75 weight percentage in the former, and 50—60 in the latter [VÖLGYI 1965]. As a local difference, it is emphashized by KLEB [1968, 1971, 1973] that the Lower Pannonian in the western Mecsek Mountains, as compared to the Sarmatian, is characterized by the quantitative decrease of the quarzite and the quantitative increase of the mica and feldspar.

LOWER PANNONIAN

The Lower Pannonian is characterized — besides the dominance of monotonous argillaceous and calcareous marls, siltes and siltstones — by that the sandstone lenses and beds loose their importance. Accordingly, its mollusc and ostracode fauna is also rather monotonous.

The earliest terrestrial vertebrate fauna of the Lower Pannonian occurs within the Monacium which corresponds to the "B" Zone of PAPP [1948—1959*b*]. This fauna that can be seemed a direct descendant of the „Upper Tortonian" ones is known sporadically (from Sopron and Diósd), and is characterized with the lack of *Hipparion* and the presence of *Anchitherium* [KRETZOI 1961, 1969].

The representatives of the second and third faunal waves of the Lower Pannonian vertebrates are unknown in Hungary so far, but these are recorded in Austria, i. e. on the western margin of the Pannonian basin. The second, hitherto unnamed phase, which can be correlated to the *Congeria partschi-* and *C. hörnesi*-bearing "*C*" and "*D*" Zones of PAPP, is characterized — besides of the restriction of the Miocene elements and the invasion of the *Hipparions* — with the survival of certain ancient types (e. g. *Anchitherium, Listriodon* and *Amphicyon;* Gaiselberg: ZAPFE [1948]; Lassnitzhöhe: MOTTL [1955], THENIUS [1959]). The third faunal phase, corresponding to the "*E*" Zone with *Congeria subglobosa*, is suggested by the findings of *Hipparion* around Brunn and Vösendorf, in which the *Anchitherium* and *Listriodon* is yet absent [KRETZOI 1969, p. 182].

The "*B*"—"*E*" beds of the Vösendorf locality has been suggested previously by the present writer, too, as the *neo-stratotype* for the Lower Pannonian [BARTHA 1971*a*, pp. 30—31, 1971*b*]. The only 20 m thick "*A*" Zone here contains still several Sarmatian elements, and the „*F*" Zone belongs to the base of the Upper Pannonian.

The water depth of the Lower Pannonian lake could not have been more than 500 m. This value was obtained by VÖLGYI [1965] using the method of SZEBÉNYI [1955], i. e. taking into account the elevation of surface, the thickness of strata, and the degree and excess of submergence. According to the present writer, it is overcalculated. On the basis of recent analogies, the water was pliohaline.

For *the basin-facies of the Lower Pannonian*, the following lithological subdivisions have been established [KŐRÖSSY 1968]. Because of the intermittent coring this subdivisioning going from above downwards has only a local value:

4. Aleuritic argillaceous marls.
3. Argillaceous marls with intercalating sandstone beds.
2. Lighter- or darker-grey calcareous marls.
1. Coastal basal-conglomerate, which, owing to its geographical position and the temporal displacement of the transgression, does not form either a continuous, or a coeval horizon. But where it occurs, this is the oldest Pannonian rock-type.

On the other hand, a litho- and biostratigraphically well established subdivisioning was elaborated for the tripartite *Lower Pannonian of the southern foreland of the Transdanubian Central Mountains* [JÁMBOR and KORPÁS—HÓDI 1971].

The separation of the grey argillaceous marls of the Lower Horizon from the Sarmatian is enabled lithologically by the basal biotitic dacite-tuff layers, and paleontologically by the small-sized, but highly mutable fossils corresponding to the „Praepontian fauna" of GORJANOVIĆ—KRAMBERGER [1890]. Among the latter ones there is a form, too, which belongs to the group of the Dacian species *Congeria neumayri* ANDR. Because of the possibility of occasional homocomorphy, this form is referred here provisionally alone as *Congeria* sp. The several small bivalves ranging into the species *Limnocardium praeponticum* KRAMB., *L. plicatiformis* KRAMB. and *L. cekuši* KRAMB. suggest undoubtedly the lowermost horizon of the Pannonian. — The fauna impoverishes in the near-shore facies; besides *Limnocardium* sp. (from the group of the *L. praeponticum*) only some specimens of *Planorbis, Micromelania* and *Hydrobia* occur.

Within the basal part of the basin facies (in some places, e. g. in borehole Csákvár-10), *diatomite beds* also appear, indicating the temporary separation of the sedimentary site [HAJÓS 1971, JÁMBOR 1971*b*].

The Middle Horizon is characterized in the basin facies with *Congeria banatica* R. HOERN., *Paradacna lenzi* R. HOERN. and *Parvidacna laevicostata* WENZ, and in the near-shore facies with *Parvidacna laevicostata* WENZ, with the appearance of *Melanopsis fossilis* MART. ET GMEL. and with the dominance of other species of *Melanopsis (Fig. 4)*.

The Upper Horizon is demonstrated both in the near-shore and basin facies with the dominance of the *Congeria czjžeki* M. HÖRN. As associated rarer elements, *Paradacna lenzi* (R. HOERN.), *P. maorti* (BARABÁS ET STRAUSZ), *Kaladacna steindachneri* (BRUS.), and even some characteristic Upper Pannonian forms (e. g. *L. rothi* HAL., *L. rogenhoferi* BRUS. and *Congeria zagrabiensis* BRUS.) also occur.

The origin of the Lower Pannonian fauna was interpreted by JÁMBOR and KORPÁS-HÓDI [1971] with the transmutation and continuous evolution of the Sarmatian fauna under the new conditions of the Pannonian. On the other hand — according to the view of the present writer — a direct speciation can be expected only at the Sarmatian/Pannonian boundary. One part of the molluscs of the "*L. praeponticum* Horizon" is namely unchanged Sarmatian survivor, indeed (e. g. *Melanopsis impressa* KRAUSS), but the other part is made up of new species, which would have generated by mutation from Sarmatian ancestors. The small-sized, variable representatives of *Limnocardium* in this horizon were originated from the Sarmatian *Cardium obsoletum* and *C. plicatum* already by GORJANOVIĆ—KRAMBERGER [1980] and LŐRENTHEY [1890], too. — But the derivation of the *Congeria banatica* from one of the Miocene species of *Congeria* in Hungary (e. g. from the *C. böckhi*), as well as the derivation of the "Adacna"-type bivalves (*P. lenzi, P. abichi* — dominating within the *C. banatica* Horizon) from the *Limnocardiums* of the "*L. praeponticum* Horizon" is improbable, even by the supposition of pleiotropic mutations. That much less because the species *L. praeponticum, L. plicatiformis* and *L. cekuši* outlive the earliest appearance of the "*Adacna*"-type bivalves, representing in this way a parallel, but shorter, "*dead-end*"-type evolutionary lineage. The contradiction included among the above presented facts can be explained — according to the present writer — by the following reconstruction. After the pre-Pannonian separation, already in the late *L. praeponticum*-time a connection brought about between the Pannonian and Dacian basins, and in this way the Dacian-Euxine-type species *Limnocardium* and *Congeria* would have invaded into the Pannonian basin, and under its favourable conditions, would have been flourished. This connection, which can be expected in the area of the recent Iron Gates is regarded as limited both in space and time. So, either because of this or in consequence of other, hitherto precisely uncharacterized minor environmental differences, the faunas of the two basins did not interchange completely.

Comprehensive stratigraphical and developmental studies about the Lower Pannonian sequence of the Great Plain and Southern Transdanubia are given by STRAUSZ [1941*b*, 1942*a,b*, 1971 and SZÉLES 1968, 1971*a,b*]. But the results of these works are rather different from those of JÁMBOR and KORPÁS-HÓDI [1971]. This can be due — apart from facies differences — to the fact, that the results of the

latters are established upon continuously cored drilling samples making mass-investigations and detailed dominance studies possible, while the former authors could rely only on imperfect data of intermittent corings. As far as these latter data show, the *L. praeponticum*-fauna is unrecorded from the Great Plain. The counterparts of the basin-facies of the Lower Pannonian investigated by JÁMBOR and KORPÁS-HÓDI are constructed here by the beds with *C. banaticha* and *P. lenzi*, while those of the near-shore facies by the strata with *C. partschi* and *C. ornithopsis*, respectively.

Conclusively, the correlation between the recently existing three subdivisioning is a task of the future.

Some species of *Silicoplacentina* (Testacea, Thecamoeba) were regarded till now as characteristic forms of the higher Lower Pannonian [KŐVÁRY 1956]. However, according to SZÉLES [1971a], the *S. hungarica* KŐVÁRY appears between 1305 and 1310 m of the borehole *Szank—6*, in the *Dreissena auricularis*-bearing, so-called „transitional beds". This suggests an Upper Pannonian survival of the *Silicoplacentina*, a genus with Lower Pannonian abundance.

UPPER PANNONIAN

The Upper Pannonian sequences — as compared to prevailingly pelitic ones of the Lower Pannonian — are more diversified, and are developed cyclically in the SE foreland of the Transdanubian Central Mountains and in other places, too. These cycles start with coarse sand (occasionally with gravel), then, after repeated alternations of sand, aleurite, clay and clay-marl, end with pelitic rock-types. The four subsequent cycles of the Upper Pannonian of Central-Transdanubia is characterized with the graditional decrease in the average grain-size and the change in the composition of the fossil assemblages too [JÁMBOR and KORPÁS-HÓDI 1971]. Lignite beds and *Arenicola*-burrows are most common in the middle, oscillatory part of the sequence. On the marginal parts the closing members embrace freshwater limestones, terrestrial fossils and occasionally products of basaltic volcanism. For this reason, the characterization of the Upper Pannonian follows separately, by the tree differentiated parts.

Lower part *(C. rhomboidea—D. auricularis—C. ungulacaprae* Horizon*)*

The Lower and Upper Pannonian faunas — at least in the beginning — are markedly different in the quality and quantity of the species and the average size of the forms. The faunal change is rather sharp and immediate. In the borehole *Csákvár-(Lovasberény)-31* the *Congeria czjzeki* M. HÖRN., dominating between 218,6 and 227,0 m, is replaced between 182,2 and 186,2 m by the *Dreissena auricularis* FUCHS and its attendants. In some places the lower part of the Upper Pannonian is poor in fauna, or unfossiliferous. In other cases such species are registered between the *C. czjzeki*- and *D. auricularis*-faunas the pioneers of which have been appeared already in the Lower Pannonian, but dominate in the Upper Pannonian (e.g. *L. majeri* M. HÖRN., *L. riegeli* M. HÖRN., *Congeria zagrabiensis* BRUS.). The record of TÓTH [1971. p. 353] on the foreland of the Vértes Mts. showing the mass-occurence of *Dreissena* in 4 km distance off the coeval shore emphasizes the quite-water basin facies of these bivalves. On the other hand, the near-shore facies of the lower Upper Pannonian is indicated by the species *Congeria rhomboidea* M. HÖRN., *C. ungulacaprae* MÜNST. or *L. schmidti* M. HÖRN.

The appearance of the *Congeria rhomboidea*, *Dreissena* and *Dreissensiomya* undoubtedly suggests the new (second) opening of the *Porta Ferrea* [STEVANOVIČ

1951—1971, BARTHA 1971*a*]. But the accompanied transgression was associated with water-shallowing. Despite of the greatest extension the lake expected that time, the maximal depth of the water could have been less than 300 m. The total Late Pannonian submergence of the lake-floor, measured by the sediment thicknesses, was above 1500 m in some part-basins of the Great Plain. These movements resulted in tectonic upthrusting in certain marginal parts of the basin. In the Mecsek Mountains the temporal protraction of these Rhodanic upthurstings also can be traced. Namely these movements affected even the *Congeria rhomboidea*-bearing strata, too, containing a fauna which arrived at the Mecsek area after a certain time, through the *Porta Ferrea*, which had been opened by the first effect of the same ones.

The present writer ranges the 200 to 300 m thick, so-called "*transitional beds*", overlying the typical Lower Pannonian and cut by the *intermittently cored* boreholes of the southern Great Plain, also into the *C. rhomboidea—D. auricaularis* Horizon. The fauna yielded in these beds is constituted — besides some subordinated Lower Pannonian forms, e. g. *Congeria partschi* M. HÖRN., *C. čžjžeki* M. HÖRN. — dominantly by the aberrant varieties of the *Paradacna abichi* R. HOERN. and *P. lenzi* R. HOERN., item by *Kaladacna steindachneri* (BRUS.), *Dreissena auricularis* FUCHS, and other forms all of which has rather an Upper Pannonian character [SZÉLES 1971*a*, pp. 285—322]. The appearance of the new species and mutations is accompanied with considerable changes in the lithofacies [KŐRÖSSY 1971, p. 217], therefore the ranging of this sequence to the Lower Pannonian (loc. cit., p. 322) seems to be unjustified.

In the lower part of the Upper Pannonian the rims of the part-basins around the mountains are marked by zones of the pure quartz-sand formations [SZATMÁRI 1971]. lThese were created post-orogenetically and by repeated redeposition, under specia warm and humid climatic conditions, namely by maximal hydration an maximal outleaching of the decomposed residuum of the crumbly minerals. The derivation of one part of these lower Upper Pannonian sands around the Mecsek Mountains by disintegration and redeposition of older sediments was clearly demonstrated by comparative mineralogical studies of RAVASZ—BARANYAI [in BARTHA 1971*a*, pp. 142—144].

The neostratotype of the lower part of the Upper Pannonian was designated within the profile of the Jászberényi Street brick-yard (Kőbánya, Budapest) [BARTHA 1971*a*, p. 31, and pp. 107—108, 1971*b*; HÓDI 1966]. This is one of the rare localities where both the *C. ungulacaprae* and *C. rhomboidea* occurs in the same section, and the latter only with some metres above the former.

The vertebrate fauna of this interval was described by KRETZOI [1951, 1954, 1969, p. 182], from the Esterházy-(recently Báracháza)-cave of Csákvár (Vértes Mts.). In this biostratotype of the "Csákvárium" there is no more *Anchitherium*, even if the bulk of the species is of Miocene. However, *Hipparion* and *Microstonyx* and several other forms of the *Hipparion*-faunas are also present.

The lower part of the Hungarian Upper Pannonian can be correlated with the "*F*" Horizon of the Vienna basin.

Middle part

The middle part of the Hungarian Upper Pannonian corresponds to the "*C. balatonica-bearing sequence*" s. l. of HALAVÁTS, in which were previously included both the deeper beds yielding *Congeria balatonica* PARTSCH in great number and the overlying, practically "*C. balatonica*-free" lignite measure. The segregation of these two horizons of the sequence was firstly proposed by the present writer [BARTHA

1959*a*, *b*], having recognized their faunal, litho- and biofacial, environmental and paleogeographical differences in regional dimensions. According to him, the lower, "*C. balatonica-bearing Horizon*" of the sequence in question can be characterized, in spite of the very small water-depth, by continuous water-surface, while the upper, "*Oscillatory Horizon*" by disintegration into part-lake sand by repeated swamp-formations. These latters are accompanied with the replacement of *C. balatonica* by *C. neumayri* ANDR. The average size of the specimens, as compared to the maximum observed within the *C. rhomboidea—ungulacaprae* Horizon, decreases upwards, through the *C. balatonica-* and Oscillatory Horizons. Also the distinction between the coastal and basin-facies tends to be hardly separable upwards.

The neostratotype of this part can be designated within the Fehérpart profile of Tihany [BARTHA 1971*a*, p. 31, 1971*b*].

a) The *C. balatonica Horizon* is characterized by the dominance of the *C. balatonica* Partsch, *C. triangularis* PARTSCH and locally (e.g. in Tab) the *Prosodacna vutskitsi* (BRUS.) The drawing of its lower boundary is encumbered in the Tihany standard profile by unoutcropping of the lowermost beds, which are develop from the *C. rhomboidea—ungulacaprea* Horizon. Its upper boundary can be drawn with the first paludal intercalation. The new biostratigraphic characters of this horizon, which resulted in the doubling of the species number and the sudden appearance of the genus *Viviparus* coming from the Dacian basin was interpreted by the present writer [BARTHA 1971*a*] with the newer (i.e. *the third/reopening* of the *Porta Ferrea*).

The terrestrial vertebrate fauna corresponding to the topmost *C. rhomboidea* Horizon and to the *C. balatonica* Horizon is that called by KRETZOI [1965, 1969] as Sümegium. This fauna, in addition to the close resemblance to the SE-European *Hipparion*-fauna, yields several new Mediterranean elements (e.g. "*Pentaglis*", *Progonomys*, *Rotundomys*), as well as the younger species of some older genera.

b) The Oscillatory Horizon is one of the most characteristic and most extended sequence of the Upper Pannonian. It is known and studied — besides the exposures of the Fehérpart of Tihany, the Magaspart of Balatonkenese, the open casts for lignite in the Bükk and Mátra forelands — from several boreholes of Transdanubia and the Great Plain. This, maximally 200 m thick sequence is characterized by light-grey sand and aleurite beds intercalating with dark-brown swamp-muds, lignitic strips and seams. The number of the latters can be in some places as high as 50. It may be that thinner lignite bands occur in the earlier or later members of the Pannonian, too. But the main period of the lignite deposition in Hungary certainly falls into the *C. balatonica—C. triangularis—P. vutskitsi* Horizon, with alternation of more arid and more humid forests in the Mátra foreland [NAGY 1958]. Besides the recent forest trees, the occuring species *Daphnogene cinnamomea* (ROSSM.) KNOBL., *Engelhardtia moeriptera* (BRONG.) ETT. [PÁLFALVY 1952] and *Taxodium* sp. [BÓNA and RUMLI—SZENTAI 1966] suggest a more gentle and humid climate, as compared to that of today. A coeval lignitic deposition was general also on other areas of the Paratethys [JASKÓ 1972*a*, *b*, 1973].

Since this Oscillatory Horizon is characterized by repeated biofacies-variations, it is reasonable to draw its lower boundary at the first paludal, and its upper boundary at the first oligohaline intercalation, respectively. The newer return of the oligohaline fauna can be interpreted exclusively by combination of the process of the lagoonal filling in with crustal movements, which submerged the floors of the adjacent part-basins with temporal phase-delay. In this way the oligohaline water-

mass migrated into the basin-parts had sunk previously to greatest depth, while the retardedly submerged, filled-in, or emerged basin-parts became the sites of lignite-forming swamps. This is why the oligohaline beds of the part-basins bordered by faults of N—S or NE—SW direction cannot be correlated precisely. Owing to the at least half-phase difference, a lignitic coal seam corresponds to an oligohaline bed on the opposite side of a fault.

These tilting movements of the basinal floor seems to be proved also by the geoseizmically recognized distribution of the „boundary facies" of the Lower and Upper Pannonian [SZABÓ—KILÉNYI and SZÉNÁS 1971].

The Oscillatory Horizon can be correlated to the top of the "G" and to the "H" Horizon of the Vienna basin. As of the vertebrate fauna, this horizon corresponds to the Hatvanium of KRETZOI [1969], which has a wooded-grasslandfauna with North-Chinese, Siberian and North-Pontian affinity, and is characterized with the appearance of the genus *Cervocerus*.

The topmost, maximally 5 m thick oligohaline bed, which was suggested by the present writer [BARTHA 1971*a*, p. 150] as a well recognizable "guide bed", is characterized usually by the dominance of the species *Theodoxus vetranići* (BRUS.), *T. crenulatus* (KLEIN), *Viviparus sadleri* PARTSCH and *Melanopsis fuchsi* (HANDM.), and the occurence of the species *Congeria neumayri* ANDR., *Limnocardium soósi* BARTHA and *L. vicinum* (FUCHS). On the other hand, at Balatonszentgyörgy also the *Melanopsis bouéi* (PARTSCH) and at Tab the *Prososthenia sepulcralis* (PARTSCH) and *Prosodacna vutskitsi* (BRUS.) occurs in this guide bed, and the faunal elements of the overlying fresh-water beds differ also from the usual ones. However, this can be merely due to the natural slight differences in the process of freshening.

Upper part

The upper part of the Upper Pannonian sequence — the max. thickness of that is as high as 500—600 metres — is constituted either by freshwater (lacustrine, fluvial), or terrestrial sediments (freshwater limestone, coarse fluvial sand and aleurite, variegated clay, etc.). Its fauna consists of *Viviparus, Pisidium, Unio*, etc. Its neostratotype is the Kálvária-hill profile of Várpalota, where the "guide bed" of the Oscillatory Horizon is overlain by *Planorbarius*- and *Tachaeocampylaea*-bearing feshwater limestone wich has a 1,5 m thick intercalation of fluvial sand with "*Unio wetzleri*" (K_2 bed). However, it was recently shown by KROLOPP [in BARTHA 1972], that the species *Unio wetzleri* (DUNKER), which was originally described from the Miocene molass, is not any more represented in the Hungarian Upper Pannonian, and the Pannonian forms confounded with it belong to the East-European species *Margaritifera flabellatiformis* (GRIG.—BEREZ.).

Until recently the molluscs were have been regarded as undiagnostic for the subdivisioning the upper part of the Upper Pannonian. This can be mainly due to the fact, that the stratigraphic ranges (hemerae) of the terrestrial and fresh-water molluscs are rather long, indeed. Among the vertebrates, a fast evolution rate was found only in the family of *Arvicolidae* [KRETZOI 1969]. The established faunal waves are as follows: Baltavárium [KRETZOI 1959*a*], Estramontium [JÁNOSSY 1972], Ruscinium [KRETZOI 1962], Csarnótanum [KRETZOI 1959*b*, 1962, KRETZOI and KROLOPP 1972]. The first who — by considering both the qualitative distinction and the quantitative repartition of species — succeeded in extend the analysis applied on the small vertebrates also to the molluscs, was KROLOPP. The correlation established by him upon molluscs is in good accordance with the small vertebrate stratigraphy [KRETZOI and KROLOPP 1972] E.g. the characteristic elements of the Mind-

szent Complex, an equivalent of the Csarnótanum on the Great Plain, are — besides the "archaic" arvicolids and *Apodemus dominans* KRETZOI — the *Dreissena polymorpha* PALLAS, an ornamented *Unio* sp., the *Vivaparus dežmanianus* BRUS., *Melanopsis* sp. and the *Tachaeocampylaea doderleini* (BRUS.).

In the outlined indiaction of the directions of ancient rivers concerned the filling-in of the Pannonian Lake are important the micromineralogical studies of MOLNÁR [1965, 1966, 1971]. On the other hand, the recognition of the contemporaneous arid-worm climate was made by LŐRINCZ [1972], on the basis of the investigation of the poor pollen material from the borehole Jászladány—1. (According to this latter author, the dominant genera *Alnus* (29%), *Gingko* (13%) and *Tilia* (12%) were still considerably associated with *Taxodium, Quercus* and *Castanea*).

PROBLEMS AND PROPOSALS

Together with the increase of the boreholes by economic causes, the informations about the sequences enlarge abruptly. However, these informations cannot be compared to the direct lithological and paleontological data supplied through unintermittent corings. Despite of this fact, it is reasonable that several authors attempted to give a lithological subdivisioning, in which the faunal elements yielded by the intermittent corings can be insert [URBANCSEK 1963, KŐRÖSSY 1968, DANK 1965]. However, the effectiveness of a correlation based upon well logging can be satisfactory in the case when the log diagrams of the intermittently cored boreholes are compared with those of the bio- and lithostratigraphically well studied, continuously cored drillings.

A large-scale subdivisioning and correlation can be made also on the basis of *the connate water salinity* of the Pannonian [KORIM 1966]. Namely the Lower Pannonian connate waters contain NaCl, those in the Lower Upper Pannonian contain $NaHCO_3$, and those in the upperpart of the Upper Pannonian $CaMg(HCO_3)_2$, respectively. On the other hand, the salinity of the connate waters is affected — besides the original environmental circumstances — by several external factor, consequently it cannot be regarded as a perfectly reliable ground for subdivisioning.

The Pannonian basin and its appendages extend to 6 different countries, accordingly the view-points of the subdivisioning of their sequences are also diverse. The correlation of the different subdivisions, which can be the ground for a uniform subdivisions, which can be the ground for a uniform interpretation of the sedimentological, environmental and faunal migrational processes, needs international cooperation of uniform standpoints, roughly according to the followings:

1. It would be important to aim at the increase of the number of the reference boreholes coring the entire section of the basin. Besides of the modern study on the materials of these boreholes, it is desirable the most detailed recollection and evaluation of the classic localities.

2. It would be useful to standardize the collection technics of the Hungarian and surrounding basinal parts, on the basis of the modern mass-investigation method. In the case of publication, it would be advisable to give information about the method of the collection and the evaluation of the studied material (e.g. it comes from intermittent or unintermittent coring; the dominance and abundance evaluation is based upon statistical method or merely estimation, etc.), why only numerical data are suitable for comparing.

3. It is most desirable to carry out the up-to-date revision of the species known from the literature as soon as possible. At least the variability limits of teh "basic species"—appearing as well preserved and in a high number of specimens—should be cleared by means of the mass-investigation to get out the nearly immense confusion of specific names at last. The following steps are proposed:

a) within a single bed, to clear the distribution of the species;
b) within a vertical profile of a single locality, to recognize the temporal ranges (hemerae) of the species;
c) in different localities, to separate the geographic craces;
d) in international summary, to take all the view-points into consideration.

The necessity of these works is well demonstrated by the great differences between the present faunal lists of the *C. rhomoidea* and *C. balatonica* Horizons of the Dacian of Rumania and the Upper Pannonian of Hungary. Namely, despite of the fact, that the increase in the species number of the Hungarian horizons can be interpreted only by the connection with the Dacian basin, the number of the common species is low. It is reasonably expected, that an international species-revision, based upon mass-investigations with respect to the whole variability range of the species would be resulted in a surprisingly high number of common species among Hungary and Rumania and Yugoslavia. This is confirmed by the specimens of the *Viviparus leiostraca* BRUS. from Öcs. Namely this species — common also in the Levantian beds of Yugoslavia — should have been ranged — on the basis of mass-investigations [BARTHA 1971*a*, pp. 53—69] — to the variability range of the *Viviparus sadleri* PARTSCH. The forms from Győrszabadhegy and Kisvaszar, which previously were determined as *Viviparus neumayri* BRUS. (common a species of the Rumanian Dacian) can be ranged similarly into the *Viviparus sadleri* PARTSCH. Accordingly, there may be numerous species appearing on the faunal lists of the different countries to-day still under several names which could be unified on the basis of their variability range into a single or few taxons.

On the other hand, it sould be accentuated expressively that the mass-investigation methods cannot be restricted only to the final (i. e. appraising) phase of the studies. Thes methods should be applied also in sampling and collecting. Namely that is the only way to decide wether really homogenous sections are comprehended by our subsequent simplifying reductions.

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LETTERS OF THE COMMISSION ON MANGANESE (IAGOD)

REPORT ON THE TECHNICAL SESSIONS OF THE COMMISSION ON MANGANESE, 4TH SYMPOSIUM OF THE IAGOD, VARNA-GOLDEN SANDS, BULGARIA, SEPTEMBER 19—25, 1974

GY. GRASSELLY and I. M. VARENTSOV
President Secretary

During the 4th Symposium of the IAGOD the Commission on Manganese organized two technical sessions. At the sessions 13 scientific papers were presented. The number of participants was over 50 persons.

Technical Session I

September 23, 1974, Hotel International, Concordia Room
Chairmen: GY. GRASSELLY (Hungary), R. RASHKOV (Bulgaria)

PROF. GY. GRASSELLY, President of the Commission on Manganese opened the session. He welcomed the participants and on behalf of the Management of the Commission on Manganese he expressed his sincerest thanks to the Bulgarian Organizing Committee for the opportunity to organize these sessions. PROF. GRASSELLY outlined the main goals of the Commission on Manganese and emphasized his hope that these sessions might be a new step in the development of the Commission's activity.

1. *Ferromanganese nodules from the Gulf of Finland;* by IGOR M. VARENTSOV, Geological Institute of the Academy of Sciences of USSR, Moscow 109 017, Pyzhevskiy pereulok 7, and A. I. BLAZHCHISHIN, Atlantic Division of Institute of Oceanology of the Academy of Sciences of USSR, Kaliningrad 236 015, Prospekt Mira 1.

Of the World Ocean Basins selected for the study of formation processes of ferromanganese ores the Gulf of Finland can be considered as a typical one with an evidently distinct source of ore-forming components.

The Gulf of Finland is a peripherical part of the Baltic Sea, where the role of the continental run-off is well displayed. On the other hand, the Gulf of Finland is connected with the open sea. The main part of metals playing a role in the formation of nodules is transported in dissolved form by the River Neva and in a lesser extent by the streams from Finland.

The largest accumulations of ferromanganese nodules were observed in Eastern and Central parts of the Gulf, in areas northward of the axial troughs. The nodules are developed in the regions of considerably weak sedimentation: on the slopes of depressions, on banks and on underwater elevations.

The main morphological types of nodules are: *a)* ferromanganese hydroxide coatings on gravels and pebbles; *b)* penny-shaped nodules; *c)* discoidal nodules; *d)* crusts; *e)* beans; *f)* buckshots.

The main constituents of the nodules are the hydroxides of iron and manganese. The iron occurs mostly in form of *X*-ray amorphous hydroxides, less frequently in form of hydrogoethite, goethite and hematite and the manganese as birnessite with minor amounts of todorokite. In some nodules patches of manganoan siderite and chlorite-like minerals can be onserved.

In the Gulf of Finland from the relatively shallow areas toward the Central Trough the amount of several components of the nodules increases e. g. CO_2: 2.00 to 3.45; Mn: 23.24 to 45.06 and on the contrary, the Fe content decreases from 60.98 to 38.78 (the values are in wt. per cent calculated on clastic-, carbonate- and silica-free basis). The content of ferromanganese compounds of lower state of oxidation is increased in this direction. These data give evidences for chemical specialization of bottom waters.

Three types of nodules can be distinguished: *a)* iron-rich (Fe: 50—76%); *b)* manganese-rich (Mn: 40—70%) and *c)* ferromanganese type of intermediate composition.

The mean composition of the nodules: SiO_2: 17,42; TiO_2: 0,48; Al_2O_3: 3,14; Fe_2O_3: 26,13; FeO: 0,38; CaO: 2,32; MgO: 1,00; MnO: 2,76; MnO_2: 21,59; Na_2O: 2,76; K_2O: 1,71; H_2O^+: 7,26; H_2O^-: 7,96; P_2O_5: 2,76; CO_2: 2,38; C_{org} : 0,97; BaO: 0,19 wt. per cent and as trace elements: Cr 17; V 68; Cu 9; Ni 35; Co 96; Zn 113 and Pb 9 (in n. 10^{-4}%).

The nodules are formed as a result of chemosorption with autocatalytic oxidation during interaction of active surfaces with component-bearing solutions, usually bottom waters. The chemical composition of bottom waters controls the content of the nodule's components. After formation of the hydroxide compounds during the post-sedimentary stages in nodules local processes of carbonate and chlorite-like mineral formation took place.

2. On the source of manganese accumulated in the stratified deposits and sediments of ocean floor; by PROF. V. R. NADIRADZE, Geological Institute of the Academy of Sciences of Georgian SSR, Zoi Ruchadze 1, Tbilisi, USSR.

Lately there have appeared works arguing against the sedimentary origin of the widely spread stratified manganese deposits.

The reviewed idea of a connection existing between manganese source and volcanism, inability to explain the absence of any indication of volcanism synchronic to the accumulation of manganese within or in the vicinity of the largest manganese basins on the earth (Nikopol, Chiatura, Varna, Molango (Mexico) and others) and the connection between the source of manganese and distant volcanism with the subsequent transportation of manganese bearing solutions by floor currents along tens and hundreds of kilometers assumed by this conception, is less convincing.

The ferro-manganese concretions assembled at the ocean floor are of great theoretical and practical importance. Owing to the work mainly of Soviet and American scientists the questions of their structure, composition and genesis have been well elucidated.

The critical analysis of the stored material permits some original conclusions concerning manganese sources, the conditions of its migration and concentration.

It has been ascertained that in the Pacific Ocean manganese is regularly increasing from the shores towards the central regions with pelagic sediments of different facies and that it is distributed in banded zones with the plan dis-

tinct from that of iron because of its greater geochemical mobility. This affinity enabling its vertical migration and enriching the concretions with manganese explains the high figures of the ratio Mn/Fe in the concretions.

The organic world of benthos and the floor slow currents washed the concretions and constantly kept them on the surface of the ocean floor.

By the radiological investigation there has been established the age of the concretion „Horizon" — 16 million years at the rate of growth of 0.01 mm in 1000 years.

There are two points of view concerning the origin of manganese in concretions and associated sediments. Some authors think that the main source of manganese in ocean is the underwater volcanism. Others attribute it to the continental drift. The first does not explain the absence of manganese accumulation at earlier and stronger phases of volcanism and the concentration of manganese in the Arctic Ocean which has never had any volcanism in it. The second does not explain the high content of cobalt, nickel, copper in ocean concretions, the absence of an intense manganese accumulation of the earlier periods and the mechanism of transportation of vast masses of manganese-bearing substances at immense distances. Both of them fail in explaining the global distribution of manganese and its sedimentation during the short interval of the tertiary period.

Our cosmogenic hypothesis (1970) based on the accretional theory of the origin of planets enables us to meet these questions. It assumes the mass fall of the meteor dust rich in manganese and accompanying metals upon the earth while crossing the strong meteor currents or nebulae during the rotation of our solar system around our galaxy.

The similarity of manganese concentration in the ocean sediments of different facies and stratified deposits together with the banded zonal distribution in the Pacific Ocean may turn an additional arguments for the advanced hypothesis.

3. Manganese occurrences in the Itacaiunas River Basin, southern Amazon region, Brazil; by WARREN L. ANDERSON, ROBERT C. DYER, Companhia Meridional de Mineracao, and DOMINGO D. TORRES, Companhia Vale de Rio Doce.

Exploration activities in the north-central Brazilian Schield have led to the discovery of three supergene-enriched manganese deposits in Precambrian metasedimentary and sedimentary rocks. Identified as the Buritirama, Sereno and Azul prospects, they are found in jungle-covered terrane in the remote Itacaiunas River Basin situated in the east-central of the State of Para.

The Buritirama and Sereno deposits have been formed by the weathering and supergene enrichment of manganiferous silicate-carbonate lenses within biotite schist of probable early to middle Precambrian age. These schists overlie a micaceous quartzite which forms pronounced ridges; each deposit consists of many discrete occurrences scattered along the crest of dip slopes of these ridges. The largest known lens is 1,400 meters long and up to 30 meters thick; most lenses appear to be much smaller. Protore at Buritirama ranges from calcmica schist to slightly schistose marble contaning pyroxmangite, rhodonite, rhodochrosite, garnet, tremolite, epidote and similar minerals, the derived manganese oxide deposits contain cryptomelane, lithiophorite, nsutite, braunite, amorphous MnO_2, clay minerals, and in Sereno only, quartz. Sur-

face indications of individual lenses are brown soils, manganiferous pisolites and boulders and sparse outcrops of massive indurated manganese oxides. The indurated manganese oxides grade rapidly downwards to the fine-grained friable mixture of manganese oxide and clay that constitutes the bulk of the crude ore. The metasedimentary rocks at Buritirama and Sereno bear the same stratigraphic relation to the underlying basement as the rocks of the iron-bearing Grao-Para group of the nearby Carajas area and may be the distal, more highly metamorphosed equivalents of that group.

Crude ore grade at Buritirama ranges from 32 to 47% Mn. Fine screening eliminates diluent clay minerals and yields a concentrate of acceptable chemical quality. Sereno ores are lower grade and of smaller grain size, and cannot be upgraded by simple size-classification methods. Both deposits are of the same genetic type as those at Serra do Navio, Amapa and Morro da Mina, Minas Gerais; the friable nature and lower grade of the Buritirama and Sereno ores reflects the abscence of massive manganese carbonate in the protore.

The Azul deposit resembles the Moanda manganese deposit in Gabon. Superficial accumulations of residual manganiferous blocks and plaquettes have been derived from the weathering and enrichment of primary manganiferous shales that belong to the Rio Fresco-Gorotire formation. This formation is an unmetamorphosed sequence of coarse to fine clastic rocks that unconformably overlies the Grao Para Group. The manganiferous shales are thought to have been deposited within a shallow lagoonal basin confined to the axial region of the synclinorium that forms the iron-bearing Serra dos Carajas district, and have themselves been affected by the complex faulting of the synclinorium. The iron formation and associated basaltic rocks of the Grao Para Group are the probable source of the manganese. The block and plaquette-bearing eluvium and down-slope accumulations of manganiferous pisolites form an east-west zone about 4.5 km in length. Manganese minerals identified are lithiophorite, cryptomelane, pyrolusite and psilomelane. Preliminary analyses show the grade of the plaquette and block detritus to range from 33 to 49,6 % Mn.

4. Manganese ores in the weathering crust of Kazakhstan, USSR; by B. M. MICHAILOV, V. G. KOLOKOLTSEV and YU. M. VOROBYEV, All-Union Research Geological Institute, USSR Ministry of Geology (VSEGEI), 72b Sredniy Prospect, Leningrad 199 026, USSR.

The bauxite-bearing suffosion-karst depressions localized at the contacts of manganiferous carbonate rocks and metasomatites were studied in Western Kazakhstan, northern part of Turgai Depression, iron ore quarries of Skolovsko-Sarbaevskiy group of mines. Manganese ore occurred along the flange and on the basement of karst conical depression on the manganiferous limestones and weathered metasomatites. The manganese ore accumulations are of 1—2 m thickness, volume weight 1 g/cm^3 and are composed of unconsolidated hydroxides of manganese (Mn up to 63.7%) and iron (Fe up to 58, 0%). These accumulations of manganese ores coming down in the form of train, they are overlapped by ferruginous bauxites, ferralites and less frequently by carbonaceous clay containing remnants of Cretaceous flora.

The marked boundary between manganese ores and bauxites, the absence of manganese in bauxites and allites testify to the fact that they had been form-

ed under very different conditions. Judging from the rock relationships manganese ores had been formed before the formation of bauxites took place.

Probably the same time-break between the formation of manganese weathering crust and the bauxite ones are observed in other regions of Kazakhstan.

In the south of Central Kazakhstan on the limbs of ancient Dzhailminskaya syncline Devonian carbonate and effusive rocks are outcroped. The Cretaceous weathering crust developed on these rocks are eroded. The weathering crusts formed on Dzhailmanskaya syncline are occurred on ferromangenese ores and on the enclosing carbonaceous-clayey-carbonate rocks which are survived in the weak board zones. Manganese deposits Karadzhal, Katy, Ushkatan and others are related to these zones. The thickness of the weathering crust in this area 70—100 m.

Manganocalcite, braunite, jacobsite, rhodonite ores, formed in result of sedimentary processes in Famennian age and metamorphosed later in Upper Paleozoic epoch of folding, were transformed in the weathering crusts into psilomelane-vernadite oxide ores. Enclosing rocks without their carbonate constituents (but containing entirely the initial organic matter) were altered into siliceous- clay and carbonaceous-clayey-siliceous rocks with volume weight to 1,18 g/cm^3. In some cases the volume weight is somewhat increased in result of distinct silica metasomatism, observed in slides. The newly formed quartz is the product of such reactions.

The fact that mangenese ores contain minerals with manganese of high and intermediate degree of oxidation (Mn^{4+} ; Mn^{3+}), the presence of ferric iron only (goethit, hematite) as well as the fact that content of Cu, Zn and Pb is much higher than their clark concentration for carbonate rocks (by a factor 10^2—10^5) indicate that manganese ores had been formed under alkaline (pH >8) and highly oxidized conditions.

Paleotectonic and paleogeographic environments on the territory of Kazakhstan from the Late Paleozoic to Paleogene time allow to supose that manganese weathering crusts were formed during the periods of subarid peneplanation of Kazakh Highland (Late Juressic-Lower Cretaceous) before the humid period Albian — Cenomanian.

5. Mount Brandsnuten manganese deposit; by DIRK VAN DER WEL, Mineralogisk-Geologisk Museum, Oslo, Norway.

Mt. Brandsnuten manganese deposit is located in the province of Telemark in the high-mountain range of central southern Norway. The Telemark area consists of supracrustal-, gneissic- and granitic to monzonitic rocks. Hydrothermal action has left veins with sulfide minerals, fluorite and others.

The manganese deposit occurs in a supracrustal sequence and consists of a thin band approximately 2 kilometres in length, lying within a quartzofeldspatic metasandstone. The band is discontinuous and seldom exceeds a few centimeters in width, but can be up to 2 metres wide. Close to the deposit is a body of porphyritic granite. Granitization is widespread in this area, which probably represents a deeper section of the Telemark supracrustal area from which it is sperarated by a fault. The ore body is considered to be of primary sedimentary origin. During metamorphism oxyhydroxydes were altered to manganese-oxides and -silicates (gondite). All of the present minerals in the deposit are considered to have been produced during metamorphism of later. Jacobsite, hausmannite and braunite are early phases, whereas rhodonite and

spessartine were formed somewhat later. Retrograde processes caused part of the rhodonite to be converted to spessartine. During the hydrothermal stage fluorite, rhodochrosite, native copper and others were precipitated. This stage is probably also responsible for the variations on the ratio of $(Mn+Al):(Ca+Fe^3)$ in the garnets in the metasandstone along the borders of the manganese band. The environmental conditions of high Mn contents along with varying Fe contents and Ca-metasomatism have given a unique possibility to study the variations within the compositional field of the grossular-andradite-spessartine molecules of the garnets. Electron-microprobe analyses reveal a compositional range from relatively pure spessartines through intermediate compositions towards the andradite molecule.

Some of the mineral phases formed during the hydrothermal stage have relatively high contents of REE and other heavy metals. In particular a manganese-epidote with a high MnO-content has locally a REE content in the order of 10 wt%.

Chairmen: I. M. VARENTSOV (USSR) and G. KANURKOV (Bulgaria)

6. Regularities of location of manganese formations in the USSR; by V. P. RAKHMANOV, E. M. GRIBOV, O. G. LAZUR and YU. A. KHODAK, Laboratory of Sedimentary Mineral Resources, Ministry of Geology of USSR, 17 Marii Ulyanovoy, korp., 1. Moscow V-331, USSR.

Sedimentary and volcanogenic-sedimentary Precambrian and Phanerozoic manganese formations with manganese and iron-manganese ores, that are located on the territory of the USSR, are situated on the slopes of old masses, in subplatformes, medial massifs, in edge bending flexures, miogeosynclines, eugeosynclines.

The scales of manganese ore accumulation sharply increase from Precambrian towards Kainozoic; zones of concentration of the ores are dislocated from geosyncline regions into subplatform and platform ones; in formations with the commercial accumulation of manganese ores the terrigenous sediments begin to dominate.

Paleotectonic and landscape-climatic situations greatly influenced the composition, structure and conditions of the localization of manganese formations. The map of location of manganese formations found in different regions of the Soviet Union is analysed.

The scheme of the stratigraphic distribution of manganese deposits and occurrences in the USSR with the quantitative valuation of manganese, that they contain, is adduced.

7. Mineralogy of iron and manganese ores of Western Atasu Central Kazakhstan, USSR; by M. M. KAYUPOVA, K. I. SARPAEV, Institute of Geological Sciences, Academy of Sciences of Kazakh SSR, Alma-Ata, USSR.

Iron and manganese ores of Atasu deposits are confined to a single silica-carbonate-zinc-manganese-iron ore hydrothermal sedimentary formation of Famennian age, developed within the Zhailmin synclinorium complicated by smaller faults and folds.

According to the author's investigation data, this formation represents a natural association of synchronous lens- and seam-like zinc, iron, manganese and iron-manganese (zinc- and germanium-bearing) ore bodies and substantially carbonate sedimentary rocks enclosing them, that under conditions of the

deposits mentioned have for the first time been divided into six ore facies: siliceous-carbonateous-manganous, siliceous-carbonateous ferruginous, alumosilicate-carbonateous-ferruginous (germanium-bearing), alumosilicate-carbonateous-manganous (zinc-bearing), alumosilicate-carbonate-ferruginous-manganous (zinc- and germanium-bearing) and sulphide-ferruginous (zinc-bearing).

The peculiarity of iron and manganese ores is in the development of varied textures and structures reflecting all the features of sedimentation processes and ore substance alteration. Among ore textures and structures originated during certain stages of formation of Atasu deposits, four genetic groups can be distinguished: *1)* originated in the course of sedimentation and diagenesis; *2)* formed due to metamorphism; *3)* originated in connection with hydrothermal metasomatic activity; and *4)* formed owing to hypergenic processes.

Each genetic group of textures and structures is characteristic for particular physico-chemical and geological conditions of ore substance accumulation and its further evolution under the action of diagenetic, metamorphic, hydrothermal-metasomatic and hypergenic processes.

Iron and manganeses ores of Atasu deposits are characterized by a unique set and paragenesis of rare minerals. Not only in Kazakhstan but all-over the Soviet Union are so far unknown analogues of Atasu deposits in terms of mineral composition diversity of their ores. In addition of common ore—forming iron and manganese minerals some new mineral varieties and a great number of those found for the first time in the USSR have been discovered in Atasu. The Atasu deposits are similar to those of Franklin (New Jersey, USA) and Långban and Nordmarken (Sweden) with regard to the complex of oxide carbonate, silicate with chlorine and arsenic compounds of zinc-manganese-iron, lead-manganese, boron, strontium, manganese (ferro-zinc jacobsite, zinc jacobsite, zinc hausmannite, zinc oligonite, coronadite, kentrolite, faulerite, friedelite, pyrosmalite, ferruginous friedelite, severginite, strontium piedmontite, arsenate (manganberzeliite, brandtite, sarkinite) and others.

The ore accumulation process seems to involve three stages: hydrothermal-sedimentary, hydrothermal- metasomatic and hypergenic.

8. The manganese ore deposit of Kisenge, Kamata (Western Katanga—Shaba, Zaire). Geochemical composition of the primary carbonate ore; by LOUIS DOYEN, Laboratoire de Geologie Appliquée, Univerśité Libre, 50 Av. Roosevelt, 1050 Bruxelles, Belgique.

The manganese ore deposit of Kisenge — Kamata, of Precambrian age, must be considered as being of sediimentary origin. The primary carbonate ore is mainly composed of rodochrosite and subsidiarily of spessartine, rhodonite and braunite. The primary ore is metamorphised and rich in graphitized carbon.

The geochemical study of the primary carbonate ore is mainly based on an original application of quantity determination made by atomic absorption and on the results of the quantity determinations made by emission spectrography.

The carbonate ore is characterized by:

— a very weak iron content: 0.83%,
— relatively low calcium and magnesium content, 2,59% and 1,85%, respectively,
— the presence and the relatively homogeneous distribution of minor elements within the carbonate mass: Ni: 1.420 ppm; Co: 460 ppm; Zn: 597 ppm.

The study of the partial correlations has revealed the existence of very strong connections existing between

calcium and magnesium,
nickel and zinc,
cobalt and phosphorous.

Therefore, these elements are connected two by two by precipitation.

9. Gondite occurrences in the Central Old Planina, Bulgaria; by Kr. KOLCHEVA, ZH. IVANOV, D. DIMOV, University of Sofia, Bulgaria

In Early Paleozoic rocks of Mount Bilo, Central Old Planina were found some layers of metamorphosed manganese-bearing rocks: gondites. The layer's length: 3—4 km, thickness 1—2 to 20 m.

The gondites are the massive rocks, partly with well expressed banded structure. The fresh surfaces of these rocks are of gray, pink-gray colour, but the weathered rocks are dark brown-black brown, with the fissures filled by ferro-manganese oxides, hydroxides.

The most common minerals are spessartine (50—85%) and quartz (20—50%), rhodonite is occurred less frequently, as well as the manganese carbonates and tremolite.

In fresh, unaltered gondites the manganese content: 15,82—21,86%, but in the weathered rocks: 23,90—38,23% Mn. The phase analysis gives the evidences that manganese are presented mainly in silicate form, and the minor part of this element is in the form of manganese carbonates: manganocalcite, rhodochrosite. In the rocks altered by supergene processes the amount of oxide form of manganese is increased.

The content of Co, As, Mo, Zn, and P is higher than the average clark concentrations of these elements.

All Early Paleozoic rocks of Old Planina were regionally epizonally metamorphosed. The products of this metamorphism are the gondites. Their specific features allow to consider these rocks as related to the grade of green schists (albite-muscovite-chlorite subgrade). The characteristic assemblage: rhodonite-rhodochrosite-spessartine. The initial, primary rocks were probably clastic-clay sediments enriched by pyroclastics and silica. The deposition of these sediments was synchronous with the latest acts of volcanic activity, widely developed in geosyncline basin.

Technical Session II

September 25, 1974, Hotel International, Concordia Room
Chairmen: WARREN L. ANDERSON (Brazil) and V. PANAYOTOV (Bulgaria)

10. Manganese in water and sediments of Atlantic Ocean; by E. M. EMELYANOV, Atlantic Division of Institute of Oceanology, Academy of Sciences of USSR, Prospect Mira 1, Kaliningrad 236 015, USSR.

Geochemistry of manganese were studied in the basin of Atlantic Ocean, including seas: Baltic, Black, Mediterranean. The concentration of manganese was determined by kinetic method [ORADOVSKIY, 1964. YAZIMIRSKIY *et al.*,

1971, EMELYANOV and VLASENKO, 1972] in 520 samples of sea and interstitional suspended matter, in 560 samples of water suspended matter, in stream waters of Baltic basin (20 samples) and hot spring water samples and that of lakes, streams of Iceland (12). The concentration of manganese was determined by wet chemical methods in 1060 samples of bottom sediments, and in 70 samples of them were analysed for mobile forms of Mn^{4+}. Author compiled lots of maps, sections, diagrams which allow to illustrate the main problems of supplying of Mn into ocean, concentration of this element in water, distribution in the different types of sediments and on the bottom and to identify the mineral forms of Mn in sediments.

In stream waters of Soviet Baltic area mangenese content in dissolved form: from traces to 3 mkg/l, this value is lesser than that for concentration of dissolved manganese in sea water. Manganese concentration in the studied hot springs, lakes, and streams in Iceland as well as the shallow sea water of adjoining part of ocean: traces to 7 mkg/l. In North Atlantic concentration of dissolved manganese increased from Sargasso Sea (traces to 3 mkg/l) toward the coast (9—11 mkg/l). Concentration of Mn in deep ocean waters is approximately the same as in surface ones. In Baltic Sea and in Black Sea concentrations of dissolved manganese sharply increased from surface (traces to 10 mkg/l) to the bottom (to 1050 mkg/l). In many cases the content of dissolved manganese lowered in the zone of photosynthesis and in the transition zone, in result of biological activity of plankton. The main form of manganese in sea water — presence in solution. In the waters of open ocean the mean concentration of suspended Mn: 0,01—0,05 mkg/l or 8,1—0,5% of total amounts in shallow waters of Baltic Sea mean concentration: 1—4 mkg/l or 10—50%.

In seas with hydrosulfide contamination the amount of suspended manganese increased at the border of sharp decreasing (or complete disappearance) of O_2 and presence of H_2S. The suspended material of off-shore regions and deep-seated layers of the sea water are enriched in manganese again, in the course of sorption of this element by particulated material.

In upper parts of oceanic sediments manganese concentration: traces to 3,14%, mean: 0,10%. The lowest values of Mn were determined in shelf diatom sediments (0,01%) and glauconite sediments (0,02%), the highest concentrations in red clays (0,40%). Manganese in sediments increasing (excluding volcanic regions) with the higher concentrations of the clay fraction, in these sediments extending the distance from the coast and with depth increasing. This phenomenon is the result of increasing of fraction of mobile form of Mn^{4+} (from 0—10% in near shore sediments to 30—90% in pelagic muds). Detrital form of Mn are approximately constant.

Mean concentration of manganese in volcano-clastic sediments of the North Atlantic is 0,15%, in sediments of rift zones, composed by ultramafic fragments — 0,13%. The manganese in these sediments is present mainly in detrital form.

The major source of manganese in the ocean is terrigenous material. The volcanism does play in supplying of manganese into ocean a secondary role. This role in the Atlantic is lesser than in the Pacific Ocean.

11. The Azul Manganese deposit, Serra dos Carajas area, Southern Amazon region, Brazil; by WARREN L. ANDERSON, Companhia Meridional de Mineracao, Av. Presidente Vargas 529—9°, C. P. 2857-zc-00, Rio de Janeiro, Brazil.

In the presented paper it was described a formerly unknown region of rather promising manganese ore deposits. The author showed in a very evidential form the main structural pattern of the Azul deposit, the localization of manganese mineralization in the primary carbonate strata, and particular role of relatively older metavolcanic Lower Proterozoic rocks as a source of manganese for carbonate shallow water accumulations. On the Precambrian rocks are developed the lateritic weathering crust, containing huge amounts of manganese oxide minerals, of economic importance. The special interest of the paper is the description of successive formation of manganese accumulations with the progressive enrichment of ore's grade: basic metavolcanites with notable content of manganese; — carbonate strata, containing manganocalcite, rhodochrosite ores, — laterite accumulations with high grade oxide manganese ores.

12. On the mechanism of formation of Obrochishte manganese deposit, Lower Oligocene, Varna region, Bulgaria; by I. K. NACHEV, Geological Institute of the Academy of Sciences of Bulgaria, Sofia, and LILIAN NACHEVA, NIPRORUDA, Stambolijski Squ. 205, Sofia, Bulgaria

The authors presented data on structure, mode of occurrences of Lower Oligocene manganese deposit Obrochishte. The ores are represented by two main phases: carbonate (calcium-rhodochrosite-manganocalcite) and manganese silicate minerals, composing pisolites and other sorts of globuls and in many cases clay-like cement. The lower and upper contacts of 10 m thick manganese ore horizon are of errosional unconformity. The manganese ore-bearing horizon is developed over the vast area of Paleogene depression. The approximate reserves of Mn in this region are about 2×10^9 tons of Mn. The authors suggested the sedimentary-diagenetic origin of this deposit.

13. The experimental data on the study of mechanism of manganese ore formations in recent basins; by I. M. VARENTSOV, Geological Institute, Academy of Sciences of USSR, Pyzhevskiy pereulok 7, Moscow 109 017, USSR

In the paper data of direct observation in nature on the main factors controlling the processe of formation of manganese, ferromanganese ores in Recent Basins were presented. These observation serves as a basis for the experimental researches. It was given a brief description of experiments with sea water solutions containing Mn, Fe, Ni, and Co in the form of complex compounds and added sorbents: synthetic hydroxide of Mn and Fe (δ-MnO_2; γ-FeOOH) In result of such interaction it was received newly formed hydroxide compounds of these elements, mainly as non-stoichiometric solid solutions, spinel-like compounds, depending on the relationships of amounts of this elements in the inital solution. The data obtained allow to suppose that the process are complex, multistage interaction. The following stages may be identified: 1) Ion-exchange stage of highly selective sorption, with equivalent releasing of H^+ into solution; 2) Stage of oxidation of the sorbed elements and formation of hydroxide compounds at the interphase: solid — solution; 3) Stage of dehydration, compaction and partial recrystallization.

Chemosorption plays the leading role with an autocatalytic oxidation process of accumulation of the studied transitional metals. The newly formed phases act in the subsequent cycles of interaction as active sorbents.

The papers presented at the technical sessions of the Commission on Manganese cover a wide area of the geology, geochemistry and mineralogy of manganese, and the papers delivered and the discussions thereafter may be considered as a sign of increasing interest of the geologists in the manysided and various topics of the manganese researches.

REPORT ON THE BUSINESS MEETING OF THE COMMISSION ON MANGANESE, 4TH IAGOD SYMPOSIUM, VARNA-GOLDEN SANDS, BULGARIA, SEPTEMBER 25, 1974

GY. GRASSELLY and I. M. VARENTSOV
President Secretary

The Business Meeting was chaired by PROF. GRASSELLY, President of the Commission on Manganese and the IAGOD Council was represented by DR. D. F. SANGSTER, Treasurer of IAGOD, Secretary: Dr. I. M. VARENTSOV, Secretary of the Commission on Manganese. About 30 persons attended the Business Meeting.

The Chairman welcomed the participants and proposed for discussion the following agenda:

1. Report of the Secretary on the activity of the Commission since the Montreal Meeting:
   a) Information on the organization of the 2nd International Symposium on the Geology and Geochemistry of Manganese during the 25th IGC to be held in 1976, Sydney, Australia,
   b) Information on the present stage of organization of an International Monograph on the Geology and Geochemistry of Manganese,
2. Election of Officers of the Commission on Manganese for the period 1974—1978.

The agenda proposed by the chairman were accepted by the Business Meeting. The Secretary submitted the reports as mentioned above.

1. The Commission on Manganese was established at the 2nd IAGOD Symposium in 1967 in St. Andrews (Scotland). The first technical session and business meeting of the Commission was organized in Tokyo-Kyoto during the IMA-IAGOD Meeting, 1970. The second ones were organized during the 24th International Geological Congress in 1972 in Montreal (Canada). According to the decisions of the Montreal Meeting the Management of the Commission on Manganese has had to solve the main tasks:

— Organization of the 3rd Technical Session and Business Meeting during the 4th Symposium of the IAGOD, 1974, Varna, Bulgaria;
— Preparation of the 2nd International Symposium on the Geology and Geochemistry of Manganese during the 25th International Geological Congress, 1976, Sydney, Australia;
— Preparation of an International Monograph on the Geology and Geochemistry of Manganese and as the first step the organization of an Editorial Board.

Details on the activity and plans of the Commission on Manganese are reported in „Letters of the Commission on Manganese (IAGOD)" published in Acta Mineralogica-Petrographica Universitatis Szegediensis, vol. XIX—XXI (1969—1973).

Considering the results of the technical sessions it may be stated that the first item of the planned program is completed.

a) Informations on the organization of the 2nd International Symposium on the Geology and Geochemistry of Manganese, 25th IGC, 1976 Australia.

General Statement; The goal of the Symposium is to review the advances on the field of manganese geology and geochemistry during the last 20 years, since the Mexican Symposium on Manganese, 20th IGC, 1956, Mexico.

The main sections of the Symposium;

Geology of Manganese Deposits,
Mineralogy and Geochemistry of Manganese,
Manganese on the Floor of Recent Basins (Geochemistry, Mineralogy,Ore Deposits and Metalliferous Muds). The session of the last section is organized as a joint session by the IAGOD Commission on Manganese and the IUGS Commission for Marine Geology, as a part of the Commission for Marine Geology Symposium: Economic Geology of the Sea Floor.

Time of the Symposium; Conforming to the proposed schedule of the 25th IGC (Ist Circular p. 7) the Symposium on the Geology and Geochemistry of Manganese could be held in the following days (1976):

August 17, Tuesday,	14.00—17.00	Technical Session
August 18, Wednesday,	14.00—16.00	Technical Session
	16.15—18.00	Business Meeting
August 19, Thursday,	14.00—17.00	Technical Session[+]
August 20, Friday,	14.00—17.00	Technical Session

([+]The programme for this day is already compiled. It will be a joint session of IAGOD Commission on Manganese and IUGS Commission for Marine Geology.)

Time allocated for the presentation of papers is 20 minutes and 10 minutes for discussion.

Detailed information on the Symposium's Programme will be prepared for publication in the 3rd Circular of the 25th IGC.

Participation in the Symposium. The Symposium on the Geology and Geochemistry of Manganese will be held in course of the 25th IGC and participation in the IGC provides the possibility for the interested persons to attend the sessions of this Symposium.

Conveners of the Symposium on the Geology and Geochemistry of Manganese;

Section I Geology of Manganese Deposits

DR. JOHN VAN N. DORR II, 6220 Wiscasset Road,
Washington, D. C. 20016, U. S. A.
PROF. DR. SUPRIYA ROY, Dept. of Geology, Jadavpur University, Calcutta 32, India

Section II Mineralogy and Geochemistry of Manganese

PROF. DR. RONALD SOREM, Dept. of Geology, Washington State University, Pullman, Washington, 99163 U. S. A.
PROF. DR. R. GIOVANOLI, Inst. für anorg. anal. und physikalische Chemie, Universität Bern, P. O. B. 140, CH-3000, Bern 9, Switzerland

Section III Manganese on the Floor of Recent Basins

DR. D. S. CRONAN, Imperial College of Science and Technology, Prince Consort Road, London SW 7 2BP, United Kingdom

PROF. DR. E. SEIBOLD, Geologisch-paläontologisches Institut der Universität Kiel, Olshausenstrasse 40/60, Kiel, F. R. G.

DR. I. M. VARENTSOV, Geological Institute, Academy of Sciences of USSR, Pyzhevskiy pereulok 7, 109017 Moscow Zh-17, USSR

The organizational work of the Commission concerning the 2nd Symposium on Manganese will be supported also by the Australian domiciled contact Representative of the Commission, DR. D. G. MOYE, Director of Exploration, The Brocken Hill Proprietary Co. Ltd., BHP House, 140 William Street, Melbourne, Victoria 3000, Australia.

The Business Meeting approved the list of conveners proposed.

b) Information on the present stage of organization of an International Monograph on the Geology and Geochemistry of Manganese and on the preparation and presentation of papers.

Preparation and presentation of papers. As it was mentioned above, the Symposium on Manganese will be organized in course of the 25th IGC. Abstracts of papers presented at the Symposium are planned to be published in the IGC Volume of Abstracts. Each contributor should submit a detailed abstract of his/her paper to the Conveners of the corresponding section BEFORE JULY 1, 1975.

After evaluating the papers submitted authors will be asked to submit the paper's manuscript BEFORE FEBRUARY 1, 1976. The papers accepted and included into the Programme of the Sections as well as further papers not delivered at the Section's Sessions, general review works reflecting the advances in the study of geology, geochemistry and mineralogy of manganese during the last 20 years may be selected for publication in the International Monograph on the Geology and Geochemistry of Manganese.

The *International Monograph on the Geology and Geochemistry of Manganese* will be published according to plan in two volumes:

Vol. I General problems (about 400 pp)
Vol. II Geology of Manganese Deposits (about 500 pp).

PROF. GRASSELLY, President of the Commission on Manganese entered into correspondence with the Publishing House of the Hungarian Academy of Sciences (Budapest) as well as with the Schweizerbart'sche Verlagsbuchhandlung (Dr. Nägele, Stuttgart, F. R. G.). July 16, 1974 the President and the Secretary, DR. I. M. VARENTSOV carried on negotitations with the Deputy Director of the Publishing House of the Hungarian Academy of Sciences concerning the publication of the Monograph planned. A very reassuring and satisfactory preliminary agreement was achieved. The Monograph will be issued by the Publishing Houses mentioned in co-operation.

After preliminary correspondence and talks with leading manganese geologists the Mangament of the Commission on Manganese makes a proposal for the *Editorial Board;*

Editor in chief: DR. I. M. VARENTSOV (USSR)
Editors: DR. D. S. CRONAN (U. K.), DR. J. E. CUDJOE (Ghana), DR. J. V. N. DORR (U. S. A.), PROF. DR. S. ROY (India), PROF. DR. R. SOREM (U. S. A.), DR. H. WALTER, (F. R. G.)
Members of the Editorial Board: PROF. DR. GY. GRASSELLY (Hungary), PROF. DR. H. PÉLISSONIER (France) , DR. V. P. RACHMANOV (USSR), PROF. DR. E. SEIBOLD (F. R. G.)

The proposal concerning the Editorial Board was approved by the Business Meeting.

2. Election of the Officers of the Commission on Manganese for the 1974—1978 period.

The chairmanship was taken over from PROF. GRASSELLY by DR. D. F. SANGSTER, representative of the IAGOD Council. On behalf of the IAGOD Council, DR. SANGSTER appreciated the activity and efforts of the Commission on Manganese which proved to be one of the most successful among the Commissions and Working Groups of the IAGOD. In the next two years the Commission on Manganese looks forward again to fairly hard duties: organization the 2nd International Symposium on Manganese and the edition of the International Monograph on the Geology and Geochemistry of Manganese. Therefore, it is proposed by the IAGOD Council that the present officers be asked to continue in their post and complete the programme started and promoted by them.

DR. SANGSTER's proposal was accepted by the Business Meeting and the Officers were elected for the period 1974—1978:

President: PROF. DR. GY. GRASSELLY (Hungary)
Vice-President: DR. JOHN VAN N. DORR (U. S. A.)
Vice-President: PROF. DR. SUPRIYA ROY (India)
Secretary: DR. IGOR M. VARENTSOV (U. S. S.R.)

After the election Prof. Grasselly, President of the Commission on Manganese expressed his gratitude to the participants of the Business Meeting for their confidence and asked for their active co-operation in the future.

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Felelős kiadó: Dr. Grasselly Gyula
74-3643 — Szegedi Nyomda